SYNTHESIS AND REACTIVITIES OF NOVEL DIVALENT GROUP 14 ELEMENTS SPECIES

WANG LILIANG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2017
SYNTHESIS AND REACTIVITIES OF NOVEL DIVALENT GROUP 14 ELEMENTS SPECIES

WANG LILIANG

School of Physical and Mathematical Sciences

A thesis submitted to the Nanyang Technological University

in fulfilment of the requirements for the degree of

Doctor of Philosophy

2017
Acknowledgements

I would first like to express my sincere appreciation to my supervisor, Nanyang Assistant Professor Dr. Rei Kinjo, for recruiting me into the research group and giving the chance to immerse myself in the research life. I should also thank my supervisor Dr. Kinjo for his guidance, patience and support throughout the years of my Ph.D study. Without his advice and help, I cannot finish my Ph.D thesis, even would never be a Doctor of Chemistry in my life.

I would always like to extend my gratitude to my colleagues in the years through the Ph.D study. I have learnt a lot of knowledge from them. Without their help, it would be tough for me. In particular, I want to thank the former members Dr. Kong Lingbing, Dr. Chong Che Chang, Dr. Cui Jingjing, Dr. Chandrakanta Dash, Dr. Kiran Kumarvarma Chakrahari, and Mr. Hu Haitao; and current members Dr. Wang Baolin, Dr. Lu Wei, Dr. Rao Bin, Dr. Su Yuanting, Mr. Wu Di, Mr. Su Bochao, and Ms. Gillian Goh Kor Hwee.

I would like to express my sincere thanks to Dr. Li Yongxin and Dr. Rakesh Ganguly for their expertise in X-ray crystallography analysis. I am also thankful to Ms. Goh Ee Ling and Mr. Keith Leung for their kind assistance in NMR analysis. I am grateful to appreciate the supports and help from all staffs in CBC.

I would also like to appreciate the Nanyang Technological University, Singapore (NTU) for giving me the opportunity to pursue my degree and awarding me a research scholarship.

I should finally thank my father Mr. Wang Yuhe, my mother Mrs. Du Yumei, and my young sister Ms. Wang Xinyue for their supports and encouragement throughout the four years.
Table of Contents

Acknowledgements .................................................................................................................. I
List of Abbreviations ................................................................................................................ IX
List of Schemes ........................................................................................................................ XI
List of Figures .......................................................................................................................... XV
List of Tables ........................................................................................................................... XVIII
Abstract ........................................................................................................................................ XIX

Chapter 1 General Introduction

1.1 A brief history of stable divalent species of Group 14 elements ........................................ 1
   1.1.1 A brief history of carbenes ............................................................................................. 1
   1.1.2 Group 14 metallylenes .................................................................................................. 4
1.2 The reactions of divalent species of Group 14 elements (C-Ge) ............................................ 9
   1.2.1 Insertion of divalent species of Group 14 elements into σ bonds ................................. 9
   1.2.2 Addition of Group 14 divalent species to π bonds ....................................................... 11
   1.2.3 Oxidation reactions of divalent species of Group 14 elements .................................... 15
   1.2.4 Coordination of metallylenes to transition metals ....................................................... 17
1.3 Project Objectives ................................................................................................................ 20
1.4 References .......................................................................................................................... 21

Chapter 2 Synthesis & Characterization of a Cyclic (Alkyl)(amino) germylene

2.1 Introduction .......................................................................................................................... 29
2.2 Results and Discussions ...................................................................................................... 35
   2.2.1 Comparison of molecular orbitals of germynes (VIII’, IX’, XI’, and 1’) ........... 35
   2.2.2 Preparation of cyclic (alkyl)(amino) dichlorogermane 4 ........................................ 36
   2.2.3 Synthesis of cyclic (alkyl)(amino) germylene 1 ....................................................... 39
2.3 Conclusion ............................................................................................................................. 43
Chapter 3 Oxidation and related reactivity of cyclic (alkyl)(amino) germylene with N₂O, S₈ and TEMPO

3.1 Introduction ........................................................................................................... 55
   3.1.1 Intramolecular base stabilization of germanthione ........................................... 55
   3.1.2 Intermolecular base stabilization of germanone .............................................. 57
   3.1.3 Steric-stabilization of germanone and germanthione ....................................... 58
3.2 Results and Discussions ......................................................................................... 59
   3.2.1 Reaction of germylene 1 with S₈ .................................................................. 59
   3.2.2 Reaction of germylene 1 with N₂O ................................................................. 64
   3.2.3 Reaction of germylene 1 with TEMPO ......................................................... 65
3.3 Conclusion ............................................................................................................... 67
3.4 Experimental Section ............................................................................................. 68
   3.4.1 General Information ....................................................................................... 68
   3.4.2 Reaction of germylene 1 with S₈ .................................................................. 68
   3.4.3 Reaction of germylene 1 with gallium trichloride .......................................... 69
   3.4.4 Reaction of germylene 1 with nitrous oxide ................................................... 69
   3.4.5 Reaction of germylene 1 with TEMPO ......................................................... 70
   3.4.6 ¹H and ¹³C NMR Spectra ............................................................................. 71
Chapter 4 Equilibrium of silylium exchange: germyle activation of hydrosilanes under $B(C_6F_5)_3$ catalysis

4.1 Introduction ....................................................................................................................... 79
  4.1.1 Activating the Si−H bond in hydrosilanes by carbenes ........................................... 79
  4.1.2 Activating the Si−H bond in hydrosilanes by silylenes ............................................. 81
  4.1.3 Activating the Si−H bond in hydrosilane by germyle ............................................. 82

4.2 Results and Discussions ................................................................................................. 86
  4.2.1 Reaction of germyle 1 with hydrosilanes ................................................................. 86
  4.2.2 Synthesis of modified germyle 7 ............................................................................. 89
  4.2.3 Reaction of germyle 7 with hydrosilanes in the presence of $B(C_6F_5)_3$ .............. 92
  4.2.4 Mechanism elucidation and kinetic studies ............................................................. 98

4.3 Conclusion ....................................................................................................................... 104

4.4 Experimental Section .................................................................................................... 105
  4.4.1 General Information ................................................................................................. 105
  4.4.2 Synthesis of imine 8 ............................................................................................... 105
  4.4.3 Synthesis of cyclic (alkyl)(amino) dichlorogermane 9 ......................................... 105
  4.4.4 Synthesis of modified cyclic (alkyl)(amino) germyle 7 ......................................... 106
  4.4.5 Reactions of hydrosilanes 2 with germyle 7 in the presence of $B(C_6F_5)_3$ ...... 106
  4.4.6 Kinetic studies ......................................................................................................... 108

4.5 Reference ....................................................................................................................... 118

Chapter 5 Reactions of germyles with metal complexes

5.1 Introduction ....................................................................................................................... 121

5.2 Results and Discussions ............................................................................................... 130
  5.2.1 Reaction of CAAGe 1 with triphenylphosphine gold(I) chloride ......................... 130
Chapter 6 Hydroamination of terminal alkynes with ammonia catalysed by 2-pyridyene gold(I) catalyst to construct pyridine derivatives

6.1 Introduction ........................................................................................................... 161
6.2 Results and Discussions...................................................................................... 169
6.3 Conclusion ........................................................................................................... 187
6.4 Experimental Section.......................................................................................... 188
   6.4.1 Synthesis of compound 3,5-bis(3,5-di-tert-butylphenyl)pyridine 2 ............. 188
   6.4.2 Synthesis of compound 3............................................................................. 188
   6.4.3 Synthesis of compound 4............................................................................. 189
   6.4.4 Synthesis of compound 1............................................................................. 189
6.4.5 Au-catalyzed construction of pyridine derivatives 7................................. 190

6.4.7 Au-catalyzed hydroimination of terminal aryl alkynes 5............................. 196

6.4.7 $^1$H, $^{13}$C and $^{19}$F NMR Spectra................................................................. 202

6.5 Reference .............................................................................................................. 242

Appendix A Crystallographic details ................................................................. 251

Appendix B Theoretical calculation ...................................................................... 261
List of Abbreviations

NMR  Nuclear magnetic resonance
δ    chemical shift
eq.  equivalent
g    gram
h    hour
IR   infra-red
J    coupling constant
s    singlet
d    doublet
q    quartet
m    multiplet
t    triplet
br   broad
Hz   Hertz
MHz  megahertz
calcd calculated
HOMO Highest Occupied Molecular Orbital
LUMO Lowest Unoccupied Molecular Orbital
P₄   white phosphorus
HRMS High Resolution Mass Spectrometry
M    concentration in mol/L
M⁺   parent ion peak in mass spectrum
mL   milliliter
mmol millimole
mol% mole percent
M.p. melting point
m/z mass to charge ratio (mass spectrum)
dec  decomposition
ppm  parts per million
r.t.  room temperature
THT  tetrahydrothiophene
THF  tetrahydrofuran
DCM  dichloromethane
L    ligands
Ad   adamantyl
Ar   aryl (substituted aromatic ring)
"Bu  n-butyl
'tBu tert-butyl
CAAC cyclic (alkyl)(amino) carbene
aNHC abnormal N-heterocyclic carbene
NHC  N-heterocyclic carbene
AAC  (alkyl)(amino) carbene
DAC  diamidocarbene
NHSis N-heterocyclic silylenes
NHGes N-heterocyclic germynes
Dipp  2,6-diisopropylphenyl
DFT  Density Functional Theory
FLPs frustrated Lewis Pairs
H    hydrogen
Me   methyl
Et   Ethyl
'iPr iso-propyl
Ph   phenyl
Mes  2,4,6-trimethylphenyl
OTf  triflate (trifluoromethanesulfonate)
List of Schemes

Scheme 1.1  a) Generation of silylene 4 and its insertion reaction; b) Generation of transient dimethylgermylene 6.................................................................5

Scheme 1.2  Synthesis of disilylgermylene 8 in solution and its dimer 9 in the solid state. ......6

Scheme 1.3  Synthesis of acyclic dicoordinated silylenes..................................................7

Scheme 1.4  a) Synthesis of the stable silylene 12; b) synthesis of the stable germylene 13.....8

Scheme 1.5  Activation of ammonia by metallylenes 13................................................10

Scheme 1.6  Synthesis of 17 and the heavier elements allenes 18. ................................10

Scheme 1.7  Reactions of stable carbenes 2 and 19 with alkynes. ................................10

Scheme 1.8  Reactions of metallylenes 13 with alkynes. ............................................11

Scheme 1.9  a) Reactions of CAAC 3 with CO; b) Stable carbenes applied for the activation of CO.................................................................13

Scheme 1.10 Reactions of germylene 25 with CO ..................................................14

Scheme 1.11 Intramolecular cyclization of NHCs 28 involving an imine moiety ..........14

Scheme 1.12 Reaction of silylenes 11 and 31 with imines ...........................................15

Scheme 1.13 Reactions of silylenes 31 with various aromatic nitriles ........................16

Scheme 1.14 The synthesis of 2H-azirines 37 and 39 via cycloaddition .................17

Scheme 1.15 Reactions of carbene 40 with chalcogens ..................................................17

Scheme 1.16 Reactions of silylene 11 with chalcogens ..................................................18

Scheme 1.17 Reactions of various carbenes with P4 ...................................................18

Scheme 1.18 Synthesis of germylene metal complexes 55 and 56. ......................21

Scheme 2.1  Synthesis of ã,ß-unsaturated imine 3 ..................................................41

Scheme 2.2  Synthesis of cyclic (alkyl)(amino) dichlorogermanium 4. .................42

Scheme 2.3  Synthesis of cyclic (alkyl)(amino) germylene 1 ......................................44

Scheme 3.1  Reaction of germylene 1 with Ss ................................................................66

Scheme 3.2  Generation of germylene 3 .................................................................68

Scheme 3.3  Reaction of germylene 1 with N2O .......................................................69

Scheme 3.4  The reaction of metallylenes with TEMPO ...........................................72

Scheme 4.1  Hydrosilane activation by CAACs I and NHC II ........................................86

Scheme 4.2  Reaction of various NHCs II with hydrosilanes ...................................86

Scheme 4.3  Proposed reaction path for the formation of Vb ..................................86

Scheme 4.4  Reactions of DAC VIII with hydrosilanes ............................................87

Scheme 4.5  Reactions of silylene XI with various silanes ........................................88

Scheme 4.6  Reversible insertion reaction of silylene XIII with hydrosilane ..........89

XII
Scheme 4.7 Reaction of cationic germylene XV with hydrosilane ........................................ 89
Scheme 4.8 Reactions of germylene/B(C6F5)3 adduct XVIII with hydrosilanes .......................... 90
Scheme 4.9 Reversible activation of hydrosilanes by B(C6F5)3 .................................................. 91
Scheme 4.10 Activation of silane 2 with germylene 1 ................................................................. 92
Scheme 4.11 Activating diphenylsilane 2a by germylene 1 in the presence of catalytic B(C6F5)3. ................................................................. 93
Scheme 4.12 Activation of triethylsilylane 2b with germylene 1 in the presence of catalytic B(C6F5)3 ................................................................. 94
Scheme 4.13 Proposed mechanism for the formation of products 4 ........................................ 94
Scheme 4.14 Synthesis of α,β-unsaturated imine 8 and dichlorogermane 9 ................................. 96
Scheme 4.15 Synthesis of germylene 7 ...................................................................................... 98
Scheme 4.16 Reaction of germylene 7 with diphenylsilane 2a .................................................... 99
Scheme 4.17 Reactions of germylene 7 with various hydrosilanes 2 ........................................ 102
Scheme 4.18 Reactions of germylene 11 with diphenyl diselenide ............................................. 105
Scheme 4.19 Reaction of germylene 7 with B(C6F5)3 or Et3SiB(C6F5)4 ........................................ 107
Scheme 4.20 Reaction of germylene 7 with Et3SiB(C6F5)4 and NaHB(C6F5)3 ............................ 108
Scheme 5.1 Synthesis of dicarbene gold(I) complexes I .......................................................... 129
Scheme 5.2 Transfer reaction between NHC tungsten complex II and (Me2S)AuCl .................. 130
Scheme 5.3 Synthesis of di-NHC gold(I) complexes II ............................................................ 130
Scheme 5.4 a) Reactions of CAACs with (Me2S)AuCl; b) reactions of complexes VIa with lithium to afford the gold(0) complex ................................................................. 131
Scheme 5.5 Synthesis of dicarbene gold(I) complex VII .......................................................... 132
Scheme 5.6 Synthesis of the first hetero-di-NHC gold(I) complex IX ....................................... 132
Scheme 5.7 Reactions of complex X with different imidazolium salts ........................................ 133
Scheme 5.8 Complexation reactions of germynes with gold(I) halides ...................................... 135
Scheme 5.9 Insertion reactions of germynes into the Au−Cl bond ............................................ 136
Scheme 5.10 Reactions of the triamidogeralithium XIV with gold(I) complexes ...................... 136
Scheme 5.11 Synthesis of bis(α-iminopyridine) germanium(II) gold(I) complex XXII .......... 137
Scheme 5.12 Reactions of CAAGe 1 with (THT)AuCl ............................................................... 138
Scheme 5.13 Reactions of CAAGe 1a and 1b with triphenylphosphine gold(I) chloride .......... 139
Scheme 5.14 Reaction of CAAGe 1 with NHC gold(I) chloride .................................................. 140
Scheme 5.15 Reactions of germanium gold(I) complexes 4a with silver reagents ................... 143
Scheme 5.16 Formation of germylene metal complexes XXIV .................................................. 145
Scheme 5.17 Reactions of germylene XXIII with palladium(0) complexes .............................. 146
Scheme 5.18 Reaction of dimeric germylene XXVI with Pd(0) and Pd(II) complexes ............ 146
Scheme 5.19 Reactions of CAAGe 1a with phosphine palladium complexes ......................... 148

XII
Scheme 6.1 Synthesis of pyridinium salt 4. \((R^1 = \text{Mes}, R^2 = 3,5^t\text{-Bu}_2\text{-C}_6\text{H}_3)\) ................................180
Scheme 6.2 Synthesis of 2-pyridyilene gold complex 1. \((R^1 = \text{Mes}, R^2 = 3,5^t\text{-Bu}_2\text{-C}_6\text{H}_3)\) .....181
Scheme 6.3 Hydroamination of ethynylbenzene with ammonia catalyzed by complex 1. .....182
Scheme 6.4 Synthesis of 7a from hydroamination of ethynylbenzene with ammonia. ....183
Scheme 6.5 Synthesis of pyridine derivatives. .................................................................183
Scheme 6.6 Synthesis of polysubstituted pyridines...........................................................183
Scheme 6.7 Synthesis of pyridines catalyzed by transition metals.....................................184
Scheme 6.8 Synthesis of 2,3,4,6-tetrasubstituted pyridines. ..............................................184
Scheme 6.9 The mechanism of hydroamination proposed. ................................................185
Scheme 6.10 Reaction of phenylacetylene 5a with 1-phenylethanol-imine 6a...................185
Scheme 6.11 Reaction of \(^{13}\text{C}\)-labeling phenylacetylene 5a* with ammonia..................186
Scheme 6.12 The mechanism of formation on 16 proposed.............................................192
Scheme 6.13 Reported reactions of imines with alkynes.....................................................194
Scheme 6.14 Reaction of imine 17a with alkyne catalyzed by gold catalyst 1. ....................195
Scheme 6.15 Reaction of imine 17a with diphenylacetylene catalyzed by gold catalyst 1. .....198
List of Figures

Figure 1.1 Electronic states of a carbene..............................................................................................................1
Figure 1.2 The electronic configuration of singlet carbenes with π donor substituents.................................2
Figure 1.3 Electronic structure of dichlorocarbene...............................................................................................2
Figure 1.4 The first isolable carbenes 1 and N-heterocyclic carbenes 2 .........................................................3
Figure 1.5 Stable carbenes with one π electron donor substituent.................................................................3
Figure 1.6 Stable carbenes with two π electron donor substituents.................................................................4
Figure 1.7 Stable heavy Group 14 analogues of alkenes and alkynes..............................................................7
Figure 1.8 Common cyclic metallylenes stabilized by various ligands.............................................................9
Figure 1.9 Orbital interactions involved in the insertion of metallylenes into X–Y bonds.........................10
Figure 1.10 Products generated by oxidation of silylenes with P4..................................................................18
Figure 1.11 The bonding of a metallylene to a transition metal center.........................................................19
Figure 1.12 The first NHC metal complexes......................................................................................................20
Figure 1.13 Isolated dicoordinated metal(0) complexes 53.............................................................................21
Figure 2.1 Proposed structure for germylene I: a) singlet ground state, b) triplet ground state. .....................33
Figure 2.2 Synthesis of germylene I....................................................................................................................34
Figure 2.3 Selected ionic germynenes II, III, and IV.........................................................................................34
Figure 2.4 Selected neutral germynenes V-XII..................................................................................................34
Figure 2.5 Syntheses of ionic germylene II and III............................................................................................35
Figure 2.6 Protonation of germylene IX with [H(OEt)2]2+[B(C6F5)4] in ether or [Et3Si(C6H5)]+B(C6F5)4] in benzene. ........................................................................................................35
Figure 2.7 Formation of germylene VIa by the reaction of germylene Va with diisopropylcarbodiimide. ...............36
Figure 2.8 Syntheses of germylene VII..............................................................................................................36
Figure 2.9 a) Syntheses of dialkylgermylene XI; b) the reductions of dichlorogerma...ne.........................37
precursors with KC8. ................................................................................................................................37
Figure 2.10 a) Selected CAAC XIII and NHC XIV; b) orbital diagrams of XIII and XIV. ...38
Figure 2.11 Cyclic (alkyl)(amino) germylene 1..................................................................................................39
Figure 2.12 Energy (eV) of frontier orbitals of N-heterocyclic germynes VIII’, IX’, cyclic dialkylgermylene XI’ and cyclic (alkyl)(amino) germylene 1’, calculated at the B3LYP/6-31G(d,p) level of theory....................................................40
Figure 2.13 Solid state structure of 3. .................................................................................................................42
Figure 2.14 Solid state structure of 4. .................................................................................................................43
Figure 2.15 $^1$H NMR spectra of 3 (top) and 4 (bottom). ............................................. 44
Figure 2.16 $^1$H NMR spectrum of 4. ............................................................................. 45
Figure 2.17 $^{13}$C NMR spectra of 4 (top) and 1 (bottom). ............................................. 45
Figure 2.18 Solid state structure of 1............................................................................. 46
Figure 2.19 Plots of the LUMO (left), HOMO (middle) and HOMO–1 (right) of 1 calculated at the B3LYP/6-31G(d,p) level of theory (hydrogen atoms are omitted for clarifying). ................................................................. 47
Figure 2.20 UV-visible spectrum of germylene 1 in hexane. ..................................... 48
Figure 3.1 Synthesis of germanone 1......................................................................... 61
Figure 3.2 Reaction of germylene III with S$_8$ and O$_2$. ........................................... 62
Figure 3.3 Reaction of germylene VI with S$_8$/PMe$_3$. .............................................. 62
Figure 3.4 Reaction of germylene or silylene VIII with N$_2$O. ..................................... 63
Figure 3.5 Reaction of tetrathiagermolane X with triphenylphosphine ...................... 63
Figure 3.6 Generation of germylene XIV................................................................. 64
Figure 3.7 Solid-state structures of 2a (left) and 2b (right). ....................................... 67
Figure 3.8 Comparison of the $^1$H NMR spectra. .................................................... 68
Figure 3.9 Solid-state structure of 3. Hydrogen atoms are omitted for clarity. .......... 69
Figure 3.10 Solid-state structures of 4. Hydrogen atoms are omitted for clarity. ......... 71
Figure 3.11 Solid-state structure of 5. Hydrogen atoms are omitted for clarity. ......... 73
Figure 4.1 $^1$H NMR spectrum (fitted) of the 2a and 1 mixture after 3 h at 90 °C. ....... 85
Figure 4.2 a) MOs comparison between 1 and 7; b) Plots of LUMO (top), HOMO (middle), and HOMO–1 (bottom) of 7 at the B3LYP/6-31G(d,p) level (the hydrogen atoms are omitted for clarity)........................................................................................................ 96
Figure 4.3 Solid state structures of 7 (left) and 8 (right). .......................................... 96
Figure 4.4 $^1$H NMR spectra of germylene 1 (top) and germylene 7 (bottom)......... 98
Figure 4.5 $^1$H NMR spectra of germylene 10 (top) and germylene 7 (bottom) ...... 100
Figure 4.6 Solid state structures of 10. .................................................................... 101
Figure 4.7 $^1$H NMR spectra (fitted) for the reaction of germylene 7 with Et$_3$SiH for various times (2 h (top), 7 h (middle) and 30 h (bottom)). .................................................. 102
Figure 4.8 $^1$H NMR spectrum of germylene 11c. .................................................... 103
Figure 4.9 $^1$H NMR spectra for the reaction of germylene 7 with triphenylsilane 2d in the presence of B(C$_6$F$_5$)$_3$ for 12 h (top), 24 h (middle), and 36 h (bottom)................................................. 104
Figure 4.10 Solid state structures of 12b and 12d ................................................... 105
Figure 4.11 $^1$HNMR spectra of the mixture of 7 with B(C$_6$F$_5$)$_3$ or Et$_3$SiB(C$_6$F$_5$)$_4$. ...... 107
Figure 4.12 Pseudo-first order plots for the activation of Et$_3$SiH with various equivalents of germylene 7 at 333.15 K. ......................................................................................... 109
Figure 5.1 The interactions between in-of-plane($\pi_1$) and out-of-plane($\pi_2$). .................................134
Figure 5.2 The two components of the Au−NHC bond in [NHC–Au–L] systems. .........................134
Figure 5.3 Solid state structures of 3a and 3b..................................................................................139
Figure 5.4 Solid state structures of 4a and 4b.................................................................................141
Figure 5.5 $^1$H NMR spectra of 4a and 4b....................................................................................142
Figure 5.6 Solid-state structure of 5d.............................................................................................144
Figure 5.7 Relevant contour plots of the cationic part of 5d at an isovalue of 0.03 au............144
Figure 5.8 Solid state structure of 6. .............................................................................................148
Figure 6.1 Synthesis of the first metal-carbene complex I............................................................171
Figure 6.2 Synthesis of the first carbene III. .................................................................................172
Figure 6.3 Synthesis of carbene IVa. ...............................................................................................172
Figure 6.4 Selected examples of NHCs. ..........................................................................................173
Figure 6.5 Hydroamination of alkynes with ammonia or hydrazine catalyzed by CAAC-Au(I) complexes. ..................................................................................................................174
Figure 6.6 The formation of amines and imines catalyzed by ruthenium catalyst. .................175
Figure 6.7 The formation of primary amines catalyzed by copper complexes. ....................175
Figure 6.8 The proposed mechanism of hydroamination catalyzed by CAAC-Au(I).................176
Figure 6.9 Energy level of the frontier orbitals of selected carbenes. ..................................177
Figure 6.10 Synthesis of 2-pyryldiene gold complex XV............................................................178
Figure 6.11 The new 2-pyridiliedene-gold complex 1.................................................................179
Figure 6.12 Solid state structure of 1............................................................................................182
Figure 6.13 Solid state structure of 7b (left) and 7g (right). .......................................................188
Figure 6.14 Solid state structure of 16d. .......................................................................................191
Figure 6.15 Solid state structure of 18b (left) and 18g (right). ................................................196
List of Tables

Table 6.1 Optimization of reaction conditions for the construction of pyridine 7a............. 187
Table 6.2 The construction of pyridine derivatives catalyzed by 1 from alkynes and ammonia.
........................................................................................................................................... 190
Table 6.3 Au-catalyzed three-component coupling reaction.................................................. 193
Table 6.4 Au-catalyzed hydroimination of terminal arylalkynes......................................... 197
Abstract

In this thesis, we have first synthesized a cyclic (alkyl)(amino) germylene (CAAGe) which possesses the high-lying HOMO−1 and low-lying LUMO, which was supported by DFT calculations. The reactivities have been investigated subsequently. The reaction of CAAGe with S₈ was first carried out, where led to the formation of the sulfido-bridged dimers as a mixture of two diastereomers involving Ge₂S₂ four-membered ring framework. But, when CAAGe was reacted with N₂O, and only trans product was obtained. The treatment of CAAGe with TEMPO was also performed and led to the formation of a 1:2 adduct. CAAGe was also reacted with hydrosilanes in the presence of 20 mol% B(C₆F₅)₃, where CAAGe was transformed into germynes 10 and 11 via silyl group exchange. Lastly, the reactions of CAAGe with various gold(I), palladium(0) and palladium(II) complexes have been performed. The Au−Cl bond insertion products [ClGe−Au−NHC] were further reacted with various silver reagents to afford the corresponding [Ge−Au−NHC]•X complex.

A new gold(I) complex featuring a pyrid-2-ylidene ligand was synthesized and fully characterized. It has been employed in hydroamination of alkynes with ammonia, which provided an efficient synthetic method for the construction of pyridine derivatives. It has also been utilized in the hydroimination of alkynes with imines, which indicated an apparent anti-Markovnikov regioselectivity to form 2-aza-1,3-dienes.
Chapter 1 General Introduction

1.1 A brief history of stable divalent species of Group 14 elements

1.1.1 A brief history of carbenes

Carbenes are neutral divalent species in which the carbon atom possesses six electrons in its valence shell. These species were first recognized by Geuther and Hermann in 1855. These authors proposed the formation of dichlorocarbene as an intermediate in the reaction of chloroform with potassium hydroxide.\(^1\)

Carbenes were considered diradical species (Figure 1.1, triplet state) until 1951 when Lennard-Jones and Pople hypothesized that carbene could exist in both singlet and triplet states.\(^2\)\(^-\)\(^3\) Seventeen years later, Hoffmann et al. described the difference between the triplet and singlet states of carbenes (Figure 1.1).

![Figure 1.1 Electronic states of a carbene.](image)

Hoffmann et al. suggested that the enhanced stability of singlet carbenes might be attributed to the \(\pi\)-overlapping between the empty \(p\) orbital of the carbene carbon and the \(\pi\) electrons of the adjacent electron withdrawing substituents, as well as their \(\sigma\)-electronegativity effect such as N, O, halogen etc. (Figure 1.2).\(^4\)-\(^7\)
For example, dichlorocarbene (Cl₂C::) is a reactive intermediate in organic synthesis in its singlet state, and has been detected by IR spectroscopy at low temperatures (Figure 1.3).

Carbenes were originally regarded as transient species until the free [bis(diisopropylamino)phosphino]trimethylsilylcarbene 1 was successfully synthesized and isolated by Bertrand et al. in 1988. In 1991, N-heterocyclic carbenes (NHCs) 2 were reported by Arduengo et al. (Figure 1.4) and have since become the most widely investigated type of singlet carbenes.
Figure 1.4 The first isolable carbenes 1 and N-heterocyclic carbenes 2.

Subsequently, the chemistry of heteroatom-stabilized singlet carbene has seen dramatic developments and the effect of the adjacent substituents on the properties of these carbenes has been studied in detail. Carbenes can be classified into two categories based on the number of adjacent substituents and their electronic properties. The first category is comprised of carbenes that possess only one π electron donor substituent (Figure 1.5). This includes (alkyl)(amino)carbenes (AACs) which are known to react with CO to yield amino ketenes. Other examples of this category include cyclic (alkyl)(amino) carbenes (CAACs). CAACs exhibit strong electrophilic and nucleophilic properties and can react with small molecules such as CO, H₂, and NH₃. Abnormal N-heterocyclic carbenes (aNHCs) are strong electron donor ligands that can activate CO₂ similar to CAACs to afford betaines.

The second category is composed of carbenes that contain two π electron donor substituents. A representative example of this category is NHCs, which are also the most prevalent singlet carbenes (Figure 1.6). NHCs show poor electrophilicity, but are strong σ donors (even stronger than the electron rich trialkylphosphines). These carbenes are amphoteric because
of the presence of an empty $p$ orbital and an occupied $s$ orbital. NHCs are used as ligands in transition metal complexes and are relevant to catalytic reactions.\textsuperscript{31,33} Such carbenes can also stabilize the low valent main group species.\textsuperscript{34-45}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{carbenes.png}
\caption{Stable carbenes with two $\pi$ electron donor substituents.}
\end{figure}

### 1.1.2 Group 14 metallylenes

Group 14 metallylenes such as silylene ($R_2Si:)$, germylene ($R_2Ge:)$, stannylene ($R_2Sn:)$, and plumbylene ($R_2Pb:)$ are heavier carbene analogues that are also neutral and divalent with six electrons in the valence shells of Si, Ge, Sn, and Pb atoms.

Silylenes have many striking similarities with germynes in terms of their synthetic route, reactivity, and geometry. Thus, the chemistry of silylene is also a means to understand that of germylene.\textsuperscript{46} Meanwhile, stannylene ($R_2Sn:)$ and plumbylene ($R_2Pb:)$ have not been discussed in this chapter because they are thermodynamically stable under ambient conditions and lack representative reactivity.

In contrast to carbenes, metallylenes exist preferably in the singlet state\textsuperscript{46-47} owing to a gradually increasing singlet-triplet energy difference ($\Delta$Est). $\Delta$Est of $H_2E: (E = C, Si, Ge, Sn,$ and Pb) increases on descending down the group, from $-9.0$ kcal mol$^{-1}$ for $H_2C:,$ 21.0 kcal mol$^{-1}$ for $H_2Si:,$ 23 kcal mol$^{-1}$ for $H_2Ge:,$ 24 kcal mol$^{-1}$ for $H_2Sn:,$ and 37 kcal mol$^{-1}$ for $H_2Pb:.$ There are mainly two reasons why carbenes may prefer to exist in the triplet state, i.e., either the magnitude of $\Delta E_{st}$ is small and/or the extent of repulsion between the two paired electrons in the $s$ orbital of metallylenes decreases upon descending the Group 14 due to the progressively
increasing radius of the $s$ orbital.$^{48,54}$

The first transient silylene 4 was observed by Skell and Goldstein in 1964 in the Si–H insertion reaction of dimethylsilylene 4 with trimethylsilane (Scheme 1.1a).$^{55}$ The transient dimethylgermylene 6 could be generated either via thermolysis or via photolysis of 7-germanorbornadienes (Scheme 1.1b).$^{56-60}$

![Scheme 1.1](image)

**Scheme 1.1** a) Generation of silylene 4 and its insertion reaction; b) Generation of transient dimethylgermylene 6.

In 1985, Apeloig *et al.* performed theoretical calculations to study the influence of different substituents on the properties of silylenes. It was found that electronegative substituents increase the energy gap between the HOMO and LUMO while $\sigma$ donors (such as Me, SiMe$_3$, and SiH$_3$) decrease this energy gap.$^{61-63}$ These results have helped experimental chemists to access the stable and isolable metallylenes.

The first isolable dicoordinated germylene 7 stabilized by electronegative substituents was obtained by Harris *et al.* in 1974.$^{64}$ They employed the reaction of GeCl$_2$·dioxane with the appropriate lithium amide (Li(NR$_1$R$_2$)) to generate acyclic diamino germylene 7 (Scheme 1.2). Germylene 7 was further utilized for the synthesis of the first acyclic disilylgermylene 8.$^{65}$ In the solid state, 8 formed a dimeric structure to give the digermene 9, which can be considered as a heavy homonuclear analogue of alkenes.
Scheme 1.2 Synthesis of disilygermylene 8 in solution and its dimer 9 in the solid state.

In 2012, Power et al.\textsuperscript{66} and Aldridge et al.\textsuperscript{67} independently reported two different types of acyclic dicoordinated silylenes 10 and 11 that were found to be stable at ambient temperature (Scheme 1.3). To date, no stable acyclic diaminosilylene has been reported.\textsuperscript{68}

\begin{align*}
\text{Scheme 1.3} \quad \text{Synthesis of acyclic dicoordinated silylenes.}
\end{align*}

Several stable heavy Group 14 analogues of alkenes R\textsubscript{2}E=ER\textsubscript{2} and alkynes RE=ER (E = Si, Ge, and Sn) (Figure 1.7) have been obtained, which are typically formed from the homocoupling of corresponding divalent species because of the lack of thermodynamic and/or kinetic stability.\textsuperscript{34, 38, 48, 65, 69-79}
The reactivities of metallylenes have attracted a lot of attention to synthesize stable metallylenes. The first stable \( N \)-heterocyclic silylene \( 12 \) (NHSi) and \( N \)-heterocyclic germylene \( 13 \) (NHGe) were synthesized by West \textit{et al.} in 1994 and Herrmann \textit{et al.} in 1992, respectively. Diamino groups were employed as substituents to protect the metallylene center from dimerization (Scheme 1.4).$^{80-81}$

\textbf{Scheme 1.4} a) Synthesis of the stable silylene \( 12 \); b) synthesis of the stable germylene \( 13 \).
Since their discovery, the field of stable metallylenes has attracted significant attention. Various ligands with subtle differences in their steric and electronic characteristics have been utilized to stabilize the metallylene center (Figure 1.8).  

Figure 1.8 Common cyclic metallylenes stabilized by various ligands.
1.2 The reactions of divalent species of Group 14 elements (C-Ge)

As discussed above, the ground state of metallylenes is singlet and they are amphoteric in nature due to the filled s orbital and the vacant p orbital in their structure. They commonly undergo four categories of reactions: a) insertion into σ bonds, b) addition toward π bonds, c) oxidation, and d) complexation reactions.

1.2.1 Insertion of divalent species of Group 14 elements into σ bonds

The insertion of metallylenes into σ bonds (X–Y) such as hydrogen (H–H), ammonia (H₂N–H), and chlorosilanes (R₃Si–Cl) may proceed via two possible mechanisms, either the σₓᵧ bond or the lone pair electrons of X attack the empty p orbital of the metallylene (Figure 1.9).

Although NHCs have been known for more than three decades, most of them are inert toward the σₓᵧ bond of ammonia due to the insufficient π acceptor ability of the carbene carbon that arises because of two adjacent nitrogen donors. However, cyclic (alkyl)(amino) carbenes can be used for the activation of ammonia (Scheme 1.5a). Meanwhile, metallylenes also show reactivity toward the activation of ammonia. Roesky et al. have utilized metallylenes featuring β-diketiminato ligands in order to perform the activation of ammonia, which resulted in different products, 14 and 15 (Scheme 1.5b).
Scheme 1.5 Activation of ammonia by metallylenes 13.

The reaction of metallylenes 16 with tetrachlorosilane and germanium tetrachloride was carried out by Kira and co-workers to obtain 17. The reduction reactions of 17 with potassium graphite were carried out to obtain the heavier analogues of allenes 18, which could be considered as silicon(0) and germanium(0) stabilized by two homometallylenes 16 (Scheme 1.6).95-97

Scheme 1.6 Synthesis of 17 and the heavier elements allenes 18.

The reactions of metallylenes with H–Si, Cl–C, and H–C bonds are quite common and have not been discussed in detail here (for more information, please see the cited references).46, 68, 91-92, 98
1.2.2 Addition of Group 14 divalent species to π bonds

The trapping reactions of transient metallylenes with unsaturated substrates such as alkenes, alkynes, and nitriles have also been reported. Similar reactions with the isolable metallylenes have been frequently employed for the synthesis of novel compounds containing heavier Group 14 elements and for the investigation of the reactivity of metallylenes. The mechanism of the addition reaction involves an interaction between the π-bond of the substrates with the empty p orbital of the divalent species in the initial step.

In carbene chemistry, only one stable carbene 19 is known to react with alkynes to form the bicyclic product 21 via a [2+1] cycloaddition. This reaction has been applied for the synthesis of cyclobutene species from both terminal and internal alkyl and aryl alkynes.\(^9^9\) When NHC 2 was utilized in the reaction with acetylene, the C–H insertion product 20 was obtained (Scheme 1.7).\(^1^0^0\)

![Scheme 1.7](image)

**Scheme 1.7** Reactions of stable carbenes 2 and 19 with alkynes.

Interesting reactions of metallylenes 13 with alkynes have been reported by Driess and co-workers. With germylene 13a, the [4+2] cycloaddition product 23b was formed in addition to the C–H insertion product 23a (Scheme 1.8a). When silylene 13b was used as the substrate, two products were formed, the insertion product 22a and the [1+2] cycloaddition product 22b.\(^1^0^1\)-\(^1^0^2\) While the reaction of silylene 24 with diphenylacetylene was carried out, the corresponding [1+2] cycloaddition product 25 was obtained in 63% yield (Scheme 1.8b).\(^9^2\)
Scheme 1.8 Reactions of metallylenes 13 and silylene 24 with alkynes.

Carbon monoxide (CO) is the simplest oxocarbon and consists of one carbon atom and one oxygen atom that is connected by a triple bond. It can be activated by transient triplet carbenes to give the corresponding ketenes. Although it is spin-allowed, very few stable carbenes have access to the activation of the CO triple bond. In 2006, Bertrand and co-workers reported the fixation of CO by CAAC 3 and AAC (Scheme 1.9a), which afforded the corresponding ketenes 26. The stable carbenes AAC, DAC, and ferrocenophane-NHC (Scheme 1.9b) have also been employed in the formation of ketenes via activation of CO.

Scheme 1.9 a) Reactions of CAAC 3 with CO; b) Stable carbenes applied for the activation of CO.
Power et al. have reported that acyclic germylene 27 react with CO (Scheme 1.10). The reaction of 27 with two equivalents of CO involved C–H insertion to afford germylenes 28 and 29.

\[
\begin{align*}
\text{Scheme 1.10} & \quad \text{Reactions of germylene 27 with CO.}
\end{align*}
\]

Imines (R₂C=NR) are important functional groups that are routinely utilized in organic synthesis. Among the reported NHC-catalyzed reactions with imines, only one addition reaction of NHCs 30 with imine has been described, in which intramolecular cyclization occurred to afford the cyclic product 31 (Scheme 1.11).

\[
\begin{align*}
\text{Scheme 1.11} & \quad \text{Intramolecular cyclization of NHCs 30 involving an imine moiety.}
\end{align*}
\]

Cycloaddition of metallylenes with imines has also been reported. Silylene 11 reacted with diimine to afford the corresponding [1+4] cycloaddition product 32 which was isolated by sublimation and fully characterized (Scheme 1.12a). Cycloaddition of dialkylsilylene 33 with various aldimines was performed by Li et al. to obtain the two products 34 and 35 in high yields. With aldmines bearing strong withdrawing groups, silaazetidines 35 were obtained via a 1,2-trimethylsilyl migration (Scheme 1.12b).
Scheme 1.12 Reactions of silylenes 11 and 33 with imines.

Li and co-workers further investigated the activation of aromatic nitriles by dialkylsilylene 33 which underwent [1+2+2] cycloadditions giving two products 36 and 37 (Scheme 1.13). It was found that when the nitrile substituted electron withdrawing groups were employed, symmetric 1,3-diaza-2-siloles 37 were formed.\textsuperscript{113}

Scheme 1.13 Reactions of silylene 33 with various aromatic nitriles.

The activation of nitriles by stable germynes has not been reported so far.\textsuperscript{114} However, its carbon analogues 1 and 40 were applicable to the [1+2] cycloaddition of stable carbenes toward nitriles, which generated 2H-azirines 39 and 41, respectively (Scheme 1.14).\textsuperscript{99,115}
Scheme 1.14 The synthesis of 2H-azirines 39 and 41 via cycloaddition.

1.2.3 Oxidation reactions of divalent species of Group 14 elements

Carbenes are readily oxidized by chalcogens and this reaction is frequently employed to confirm the generation of transient carbenes. In 1995, Enders and co-workers reported the reaction of triazolylidene 42 with O₂, S₈, and selenium to generate corresponding urea derivatives 43 (Scheme 1.15).

Scheme 1.15 Reactions of carbene 42 with chalcogens.

The oxidation reaction of stable metallylenes with chalcogens has been well documented. As almost all of the stable silylenes react with chalcogens, only a representative example is given in this introduction. The reaction of silylene 11 with chalcogens afforded the corresponding centrosymmetric spirocyclic dimers 44 (Scheme 1.16) via a proposed [Si= X] double bond intermediate.
Scheme 1.16 Reactions of silylene 11 with chalcogens.

The activation of white phosphorus (P₄) by various carbenes¹¹⁸-¹²⁰ and silylenes¹²¹-¹²⁴ has also been extensively investigated. Bertrand et al. have reported the reaction of various carbenes with P₄ and it has been found that with cyclic carbenes 2 and 3, the corresponding products 46 were generated.¹¹⁹-¹²⁰ In contrast, when an acyclic carbene 45 was utilized in this reaction, product 47 was obtained (Scheme 1.17).¹¹⁸

Scheme 1.17 Reactions of various carbenes with P₄.

Various P containing compounds were thus formed by the oxidation reaction of silylenes with P₄ (Figure 1.10). Product 48 was obtained by the reaction of silylene 13 with P₄, which further reacted with another equivalent of silylene 13 to afford 49.¹²³ A few other examples have been reported by Roesky et al.¹²¹,¹²⁴ Different products were obtained in the reaction of silylenes 50 with P₄ depending on the molar ratio. With 50a:P₄ molar ratio = 6:1, the yellow product 51 was generated in 60% yield while in the reaction of silylene 52b with P₄ (molar ratio 50b:P₄ = 2:1), the purple-colored product 52 was obtained in 50% yield after work-up.
1.2.4 Coordination of metallylenes to transition metals

Metallylene transition metal complexes are organometallic compounds featuring metallylene ligands that are coordinated to the metal center. There are two types of bonding involved in their formation, namely, σ-donation of the lone pair of electrons from the ligand to the transition metal and the π-backdonation of the d electrons of the transition metal to the empty p orbital of the metallylene ligand (Figure 1.11).}

![Figure 1.11](image-url)

**Figure 1.11** The bonding of a metallylene to a transition metal center.

The NHC-metal complexes 53 and 54 (Figure 1.12) were reported as early as 1968 by Wanzlick\(^{127}\) and Öfele\(^{128}\) respectively. Various transition metal NHC complexes have been
synthesized in the subsequent decades. NHCs are excellent ligands owing to their \( \sigma \)-donor and \( \pi \)-acceptor abilities in organometallic chemistry.\textsuperscript{129-132}

![NHC complexes](image)

**Figure 1.12** The first NHC metal complexes.

Among the different NHC transition metal complexes, zero-valent mononuclear metal complexes such as 53 have been reported independently by Bertrand *et al.* and Roesky *et al.*\textsuperscript{133-138} This type of complexes are unique because the metal center stabilized by the two CAAC units is in its zero-oxidation state (Figure 1.12). Although the transition metal complexes 55 have similar C–M–C angles that are close to 180 °C, density functional theory (DFT) calculations suggest that they possess different electronic configurations. For Au, Cu, Ni, Mn, and Zn complexes, the electronic density is mainly delocalized within the CAAC units. In the case of iron and cobalt, most of the electronic density is localized on the metal center rather than the CAAC units.
Although NHCs and stable metallylenes have not been documented in the formation of metal (0) complexes, they are usually utilized to the insertion of M–X bonds. Recently, Cabeza et al. have reported that germylene 56 undergoes a ligand exchange reaction with chloro(tetrahydrothiophene) gold(I) (THTAuCl) to afford the germylene gold complex 57. However, when germylene is reacted with either AgBF\(_4\) or CuBF\(_4\), the dicoordinated germylene M(I) complex 58 is obtained (Scheme 1.13). Similar ligand exchange reactions have also been reported by Marschner et al. 140

**Scheme 1.18** Synthesis of germylene metal complexes 57 and 58.
1.3 Project Objectives

Based on the knowledge of the chemistry of Group 14 divalent species, it can be envisaged that the heavier analogues of cyclic (alkyl)(amino) carbenes (CAACs) may exhibit peculiar electronic characters, chemical and physical properties, and reactivities. This realization prompted us to develop hitherto unknown cyclic (alkyl)(amino) metallylenes.

This project focuses on the synthesis of cyclic (alkyl)(amino) metallylenes and an investigation of their reactivities. The behavior of these compounds as ligands in transition metal complexes has also been investigated. Furthermore, the performance of transition metal-metallylene complexes in catalytic hydroamination of alkynes with ammonia has been studied.
1.4 References


53. Apeloig, Y.; Pauncz, R.; Karni, M.; West, R.; Steiner, W.; Chapman, D.,


111. Haaf, M.; Schmiedl, A.; Schmedake, T. A.; Powell, D. R.; Millevolte, A. J.; Denk,


Chapter 2 Synthesis & Characterization of a Cyclic (Alkyl)(amino) germylene

2.1 Introduction

Germylene is the germanium analogue of carbene (R₂Ge:), and is favored in the singlet ground state rather than triplet ground state (Figure 2.1). In contrast to carbene, germylene prefers the 4s²4p² valence electron configuration in the germanium centre, which possesses a vacant p-orbital and a lone pair of valence orbital. Based on the theoretical calculation, the singlet-triplet separation (ΔE_{ST}) of germylene (23 kcal mol⁻¹) is higher than that of carbene (−9 kcal mol⁻¹), which indicates that the singlet state germylene is more stable than its triplet state.

![Proposed structure for germylene I](image)

Figure 2.1 Proposed structure for germylene I: a) singlet ground state, b) triplet ground state.

To date, a lot of isolable germynes have been synthesized by stabilization effects of bulky substituents and/or coordinating ligands. Germynes usually exhibit the electrophilic character in contrast to the nucleophilicity of carbenes. The seminal work was reported in 1974 by Harris and Lappert, presenting that the reaction of GeCl₂•dioxane with lithium amide (Li(NR₁R₂)) in ether afforded germylene I (Figure 2.2).
Since then, a plethora of studies on the synthesis and reactivity of isolable germylenes were reported.\(^4\)\(^-\)\(^9\) Germylenes can be summed up in two types: a) ionic germylenes \(\text{II–IV}^{10-14}\) (Figure 2.3); b) neutral germylenes \(\text{V-XII}^{15-35}\) (Figure 2.4).

These germylenes \(\text{I-XII}\) can be isolated and stored under an inert atmosphere, and their
thermal stability depends on the steric and electronic effects from the adjacent substituents of germanium centre. Germylene II was first reported by Roesky et al. in 2001, and it was prepared from β-diketiminatolithium salt II' with germanium dichloride in ether.\textsuperscript{29-30} Subsequently, Driess and co-workers reported the reduction of II with two equivalents of potassium to afford germylene III in 33% yield.\textsuperscript{14} (Figure 2.5)

\begin{center}
\includegraphics[width=\textwidth]{figure2.5.png}
\end{center}

\textit{Figure 2.5 Syntheses of ionic germylene II and III.}

Unlike other neutral five-membered germynes, cationic germynes IVa-b were synthesized in an astounding route reported by Müller and co-workers in 2009. They employed the protonation of germylene IX with HB(C$_6$F$_5$)$_4$ in diethyl ether or Et$_3$SiB(C$_6$F$_5$)$_4$ in benzene to generate corresponding cationic germynes IVa-b (Figure 2.6).\textsuperscript{11}

\begin{center}
\includegraphics[width=\textwidth]{figure2.6.png}
\end{center}

\textit{Figure 2.6 Protonation of germylene IX with [H(OEt)$_2$]+[B(C$_6$F$_5$)$_4$] in ether or [Et$_3$Si(C$_6$H$_5$)$_4$]+[B(C$_6$F$_5$)$_4$] in benzene.}

Acyclic germylene Va reacted with diisopropylcarbodiimide via an addition reaction to afford a base-coordinated germylene VIa (Figure 2.7).\textsuperscript{16} This is the only example of a synthetic route to access a tricoordinate germylene VIa from another acyclic germylene Va.
Figure 2.7 Formation of germylene VI$_a$ by the reaction of germylene Va with diisopropylcarbodiimide.

The five-membered $N$-heterocyclic germylene VII was first reported by Meller in 1989. Benzene-1,2-diamine was reacted with $^6$BuLi to afford amidinate lithium salt, after which GeCl$_2$·dioxane was added to the mixture to afford VII (Figure 2.8).$^{20-21}$ It should be noted that both acyclic germylene V and cyclic six-membered germylene XII were obtained by the reaction of amidinate lithium salt with GeCl$_2$.$^{12-13, 29-37}$

Figure 2.8 Syntheses of germylene VII.

Compound XI$'$ can be obtained by the reaction of 1,1,4,4-tetrakis(trimethylsilyl)-butane-1,4-diyl lithium salt XI$'$ with GeCl$_2$. The reduction of dichlorogermane XI$''$ with KC$_8$ afforded the first stable dialkylgermylene XI (Figure 2.9a).$^{28}$ In comparison with XI, both saturated $N$-heterocyclic germylene VIII and unsaturated $N$-heterocyclic germylene IX were synthesized by the reduction of dichlorogermane precursors (Figure 2.9b).$^{24, 26}$
Figure 2.9 a) Syntheses of dialkylgermylene XI; b) the reductions of dichlorogerme precursors with KC₈.

In contrast to XI, N-heterocyclic germynes are sterically protected by bulky groups and electronically stabilized by both π-donation and σ-withdrawing from the adjacent nitrogen atom. Nevertheless, Germylene XI is sterically protected by bulky Me₃Si-groups without the electronic protections from them. In other words, germylene XI is the least electronically perturbed among all known isolable germynes.

Most studies of germynes have been focused on N-heterocyclic germynes (NHGes). Indeed, the investigation of NHGes predated those of its counterpart: N-heterocyclic carbenes (NHCs) and N-heterocyclic silylenes (NHSis). However, few germynes have been reported to expand the diversity of cyclic germylene skeletons, including the dialkylgermylene developed by Kira and co-workers. In carbene chemistry, Bertrand and co-workers have successfully developed cyclic (alkyl)(amino) carbenes (CAACs) XIII, in which one of the adjacent amino group was replaced with a quaternary carbon compared with NHCs XIV (Figure 2.10a).
Figure 2.10 a) Selected CAAC XIII and NHC XIV; b) orbital diagrams of XIII and XIV.

The theoretical research unclosed that the HOMO of XIII (−4.9 eV) is slightly higher than that of XIV (−5.2 eV) in energy and that CAACs XIII exhibit σ-donating and π-accepting abilities stronger than those of NHCs XIV (Figure 2.10b). Bertrand et al. utilized the peculiar steric and electronic properties of XIII for the synthesis of novel low-valence main group elements species such as boron, phosphorus, antimony, silicon, and even carbon. Additionally, XIII are also great ligands for the stabilization of zero oxidation state transition metals complexes including copper, gold, iron, nickel, cobalt, manganese, and zinc.

Herein, we design a new germylene 1 (Figure 2.11), one of the amino group was replaced with a quaternary carbon complied with IX. The different reactivity and electronic property from other known germylenes have been expected. We propose that cyclic (alkyl)(amino) germylene (CAAGe) 1 features both stronger σ-donor and π-acceptor ability, which can perform some different reactions from other germylenes toward small molecules, main group elements and transition metals complexes.

Figure 2.11 Cyclic (alkyl)(amino) germylene 1.
2.2 Results and Discussions

2.2.1 Comparison of molecular orbitals of germynes (VIII’, IX’, XI’, and I’)

Prior to preparation of germylene I, we carried out a brief inspection to compare the molecular orbitals (MOs) of cyclic germynes (VIII’, IX’, and XI’) with our target germylene I’, based on the theoretical calculation at the B3LYP/6-31G(d,p) level (Figure 2.12).

![Figure 2.12](image-url)  
**Figure 2.12** Energy (eV) of frontier orbitals of N-heterocyclic germynes VIII’, IX’, cyclic dialkylgermylene XI’ and cyclic (alkyl)(amino) germylene I’, calculated at the B3LYP/6-31G(d,p) level of theory.

The calculated result indicated that the germanium lone pair of VIII’, IX’ and I’ are located at the HOMO−1, and the HOMO−1 of I’ (−6.31 eV) is slightly higher than NHGes VIII’ and IX’ in energy (Figure 2.12). Energies of the LUMOs are predominantly unoccupied p-orbital on the germanium center for all germynes VIII’, IX’, XI’ and I’, which decrease in the order IX’ > VIII’ > I’ > XI’ from −0.60 eV to −2.71 eV. By calculation, it can be concluded that the electrophilicity of germylene I’ would be enhanced for the replacement of a π-electron donating
as well as a σ-withdrawing amino group with a σ-donating alkyl group, and the nucleophilicity of the germanium center would be concomitantly raised.

2.2.2 Preparation of cyclic (alkyl)(amino) dichlorogermane 4

Our strategy for the synthesis of cyclic (alkyl)(amino) germylene is based on oxidative 1,4-addition of germylene with 1,3-diene and subsequent reduction.\textsuperscript{73-74} We envisaged that dichlorogermylene would undergo cyclization with α,β-unsaturated imine to afford a dichlorogermane precursor featuring the GeC\textsubscript{3}N five-membered ring skeleton, which could be reduced to access germylene. To validate our hypothesis, we carried out the reaction of 3,3-bis(trimethylsilyl)acrylaldehyde\textsuperscript{75} and 2,6-diisopropylaniline in Et\textsubscript{2}O, from which α, β-unsaturated imine 3 was obtained in 72% isolated yield (Scheme 2.1). The solid state molecular structure of α, β-unsaturated imine 3 was determined by single crystal X-ray diffraction analysis (Figure 2.13).

\begin{center}
\textit{Scheme 2.1} Synthesis of α,β-unsaturated imine 3.
\end{center}
Figure 2.13 Solid state structure of 3. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [º]: N1-C1 1.2789(19), C1-C2 1.464(2), C2-C3 1.352(2); N1-C1-C2 120.05(13), C1-C2-C3 126.66(14).

Treatment of a stoichiometric amount of dichlorogermylene dioxane complex with 3 in benzene successfully underwent a 1,4-addition via a redox reaction between them, which gave a cyclic dichlorogerme derivative 4 in 96% yield. The result presents the first example of 1,4-addition of Cl₂Ge: to α,β-unsaturated imine. (Scheme 2.2) A single crystal of 4 was grown in hexane at room temperature under an inert atmosphere, and the solid state molecular structure of 4 was confirmed by single crystal X-ray diffraction analysis (Figure 2.14).

Scheme 2.2 Synthesis of cyclic (alkyl)(amino) dichlorogeranium 4.
Figure 2.14  Solid state structure of 4. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ge1-N1 1.822(2), Ge1-C1 1.959(3), C1-C2 1.531(4), C2-C3 1.340(4), C3-N1 1.408(4), C1-Si1 1.909(3), C1-Si2 1.911(3), N1-Ge1-C1 94.90(11), Ge1-C1-C2 98.41(18), C1-C2-C3 119.91(3), C2-C3-N1 119.0(3), C3-N1-Ge1 107.13(18).

To compare the $^1$H NMR spectrum of 3 with that of 4, a singlet peak for Me$_3$Si group of 4 appears at 0.25 ppm, while two singlet peaks for those of 3 were observed at 0.24 ppm and 0.26 ppm.; A doublet peak for CH$_3$ of isopropyl group of 3 appears at 1.18 ppm, while it is separated to a doublet of doublets appearing at 1.17 ppm and 1.35 ppm for 4. It means that 4 has a planar symmetric structure. There is a significant difference on the C(sp$^3$)H protons: two doublet peaks appear at 7.39 ppm and 8.15 ppm for 3, but at 4.63 ppm and 6.34 ppm for 4. (Figure 2.15)
2.2.3 Synthesis of cyclic (alkyl)(amino) germylene 1

A mixture of 4 and three equivalents of potassium graphite (KC₈) was heated at 60 °C in benzene. After work-up, germylene 1 was isolated as a dark red solid in 90% yield. (Scheme 2.3)

In the ¹H NMR spectrum of 1, a singlet for Me₃Si group appears at 0.21 ppm, which is identical to that (0.22 ppm) of 4 (Figure 2.16). The ¹³C NMR spectrum of 1 displays two peaks at 118.9 ppm and 146.7 ppm for the C(sp²)-H carbon atoms in the GeNC₃ five-membered ring, which are significantly shifted downfield in comparison to those (99.0 ppm and 139.1 ppm) of 4. (Figure 2.17)

Scheme 2.3 Synthesis of cyclic (alkyl)(amino) germylene 1.
Figure 2.16 $^1$H NMR spectrum of 4.

Figure 2.17 $^{13}$C NMR spectra of 4 (top) and 1 (bottom).

The solid state molecular structure of germylene 1 was determined by single crystal X-ray diffraction analysis (Figure 2.18). Five atoms in the GeNC$_5$ five-membered ring of 1 and 4 are coplanar (the sum of internal pentagon angles = 539.91 and 539.34 º), and 2,6-diisopropylphenyl ring at the N1 atom and the
GeNC₃ skeleton are nearly perpendicular to each other. The Ge1–N1 bond (1.859(11) Å) and the Ge1–C15 bond (1.998(14) Å) distances are slightly longer than those (Ge1–N1 1.822(2) Å, Ge1–C1 1.959(3) Å) of 4 (Figure 2.14). The N1–Ge1–C15 bond angle of 86.5(5) ° in 1 is acuter than the N1–Ge1–C1 bond angle (94.90(11) °) in 4, the corresponding N–Ge–N bond angle (84.8(1) °) in VIII₂⁴ as well as the corresponding C–Ge–C bond angle [90.97(9) °] in X₂⁸.

![Figure 2.18](image)

**Figure 2.18** Solid state structure of 1. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ge1-N1 1.859(11), Ge1-C15 1.998(14), C14-C15 1.466(19), C13-C14 1.390(13), C13-N1 1.410(16), C15-Si1 1.907(11), C15-Si2 1.876(6); N1-Ge1-C15 86.5(5), Ge1-C15-C14 106.6(6), C13-C14-C15 117.8(11), C13-C14-N1 113.8(11), C13-N1-Ge1 115.3(6).

To gain insight into the electronic features, we carried out quantum chemical calculations on 1 at the B3LYP/6-31G(d,p) level. A lone-pair orbital at the Ge atom was found in the HOMO−1, whereas the HOMO displays a Ge–N π-bonding involving the two C–Si σ-bonds which exhibit anti-bonding conjugation with the π-orbital of the C=C moiety (Figure 2.19). The LUMO is mainly the empty p orbital of the Ge center. Natural bond orbital (NBO) analysis gave Wiberg bond index (WBI) values of the Ge–N bond (0.78) and the Ge–C bond (0.73), indicating single bond nature of these bonds. Natural population analysis (NPA) manifested the second order perturbation energy of 33.97 kcal mol⁻¹ for the interaction between a lone-pair on the N atom and formally unoccupied p-orbital of the Ge atom.
Figure 2.19 Plots of the LUMO (left), HOMO (middle) and HOMO-1 (right) of 1 calculated at the B3LYP/6-31G(d,p) level of theory (hydrogen atoms are omitted for clarifying).

A UV-vis spectrum of 1 in hexane exhibits a broad peak with λ<sub>max</sub> at 368 nm, which is due to HOMO-LUMO transition, responsible for the dark red colour of 1 (Figure 2.20).

Figure 2.20 UV-visible spectrum of germylene 1 in hexane at room temperature.
2.3 Conclusion

In conclusion, we have developed a direct approach for the synthesis of a dichlorogermaine derivative 4 featuring the five-membered GeNC₃ ring skeleton through a simple 1,4-addition of dichlorogermylene•dioxane complex with α,β-unsaturated imine 3. Subsequently, the reduction of 4 with KC₈ gave cyclic (alkyl)(amino) germylene (CAAGe) 1 possessing the high-lying HOMO−1 and low-lying LUMO, which was supported by DFT calculations.

2.4 Experimental Section

2.4.1 General Information

All reactions were performed under an atmosphere of argon by using standard Schlenk or dry box techniques; solvents were dried over Na metal, K metal or CaH₂. All the substrates were obtained from the commercial sources or synthesized following literature procedures. Analytical thin layer chromatography was performed on triethylamine deactivated 0.25 mm silica gel 60-F254. Visualization was carried out with UV light. ¹H, and ¹³C spectrum were obtained with AVIII 400MHz BBFO1 spectrometer at 298 K. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Coupling constants J are given in Hz. Electrospray ionization (ESI) mass spectrum was obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with an OpticMelt Stanford Research System.

2.4.2 Synthesis of imine 3

2,6-diisopropylaniline (55 mmol, 9.75 g) and 3,3-bis(trimethylsilyl)acrylaldehyde (50 mmol, 10.00 g) were mixed in ether (100 mL). The mixture was refluxed overnight. After cooling to room temperature, the product was purified by silica gel column chromatography
(petroleum ether/ethyl acetate = 10:1) to afford 3 as a yellow solid (12.9 g, 72%). Mp: 109 °C; 

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.13 (d, $J = 10.1$ Hz, 1H, CH$_2$), 7.36 (d, $J = 10.1$ Hz, 1H, CH$_2$), 7.18 – 7.07 (m, 3H, Ar-H), 2.91 (dt, $J = 13.7, 6.9$ Hz, 2H, CH$_2$), 1.17 (s, 6H, CH$_3$), 1.15 (s, 6H, CH$_3$), 0.24 (s, 9H, Si(CH$_3$)$_3$), 0.21 (s, 9H, Si(CH$_3$)$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.40 (CH), 162.04 (CH), 151.12 (CH), 148.79 (CH), 137.23 (CH), 124.26 (CH), 122.96 (CH), 27.73 (CH), 23.61 (CH$_3$), 2.39 (Si(CH$_3$)$_3$), 0.05 (Si(CH$_3$)$_3$); HRMS (ESI): m/z calcd for C$_{21}$H$_{38}$NSi$_2$Ge: 359.2465 [(M+H)]$^+$; found: 359.2468.

2.4.3 Synthesis of cyclic (alkyl)(amino) dichlorogermane 4

(E)-N-(2,6-diisopropylphenyl)-3,3-bis(trimethylsilyl)prop-2-en-1-imine 1 (4 mmol, 1.42 g) and dichlorogermadiyl dioxane (4 mmol, 0.93 g) were mixed in benzene (20 mL). The mixture was stirred at room temperature overnight and then vacuumed to remove the solvent. The product 4 was obtained as a yellow solid (1.93 g, 96%). Mp: 154 °C; $^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.15 – 6.88 (m, 3H, Ar-H), 6.30 (d, $J = 6.3$ Hz, 1H, CH$_2$), 4.60 (d, $J = 6.3$ Hz, 1H, CH$_2$), 3.48 (dt, $J = 13.7, 6.9$ Hz, 2H, CH$_2$), 1.31 (d, $J = 6.9$ Hz, 6H, CH$_3$), 1.14 (d, $J = 6.9$ Hz, 6H, CH$_3$), 0.22 (s, 18H, Si(CH$_3$)$_3$); $^{13}$C NMR (100 MHz, C$_6$D$_6$) δ 147.82 (CH), 139.06 (CH), 137.11 (CH), 127.91 (CH), 124.04 (CH), 98.98 (CH), 33.96 (CH), 28.04 (CH), 25.72 (CH$_3$), 23.06 (CH$_3$), 0.47 (Si(CH$_3$)$_3$); HRMS (ESI): m/z calcd for C$_{21}$H$_{38}$NSi$_2$Cl$_2$Ge: 504.1132 [(M+H)]$^+$; found: 504.1156.

2.4.4 Synthesis of cyclic (alkyl)(amino) germylene 1

7 (2 mmol, 1.02 g) and KC$_8$ (6 mmol, 0.81 g) were mixed in benzene (30 mL). The mixture was stirred at 60 °C for 6 h. After stirring for another 30 min at room temperature, the mixture was filtered and concentrated under vacuum. The product 1 was obtained as a dark red solid (0.78 g, 90%). Mp: 95 °C; $^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.22 (d, $J = 4.1$ Hz, 1H, CH$_2$), 7.22 – 7.21 (m, 3H, Ar-H), 6.08 (d, $J = 4.1$ Hz, 1H, CH$_2$), 3.25 (dt, $J = 13.8, 6.9$ Hz, 2H, CH$_2$), 1.21 (d, $J = 6.9$ Hz, 6H, CH$_3$), 1.17 (d, $J = 6.9$ Hz, 6H, CH$_3$), 0.21 (s, 18H, Si(CH$_3$)$_3$); $^{13}$C NMR (100 MHz, C$_6$D$_6$) δ 147.10 (CH), 144.88 (CH), 127.82 (CH), 127.28 (CH), 123.69 (CH), 119.35 (CH), 25.72 (CH$_3$), 23.06 (CH$_3$), 0.47 (Si(CH$_3$)$_3$); HRMS (ESI): m/z calcd for C$_{21}$H$_{38}$NSi$_2$Cl$_2$: 504.1132 [(M+H)]$^+$; found: 504.1156.
28.34 (CH), 25.35 (CH₃), 24.23 (CH₃), 2.18 (Si(CH₃)₃); UV-vis (Hexane, 298 K) with λ<sub>max</sub>/nm at 368 nm; HRMS (ESI): m/z calcd for C<sub>21</sub>H<sub>38</sub>NSi₂Ge: 434.1755 [(M+H)]<sup>+</sup>; found: 434.1761.
2.4.5 $^1$H and $^{13}$C NMR Spectra

**Figure 2.21** $^1$H NMR spectrum of 3

**Figure 2.22** $^{13}$C NMR spectrum of 3
Figure 2.23 $^1$H NMR spectrum of 4

Figure 2.24 $^{13}$C NMR spectrum of 4
Figure 2.25 $^1$H NMR spectrum of 1

Figure 2.26 $^{13}$C NMR spectrum of 1
Figure 2.27 $^1$H-$^{13}$C HSQC spectrum of 1.
2.5 References


Stannylenes and Plumbylenes. In Organometallic Compounds of Low-Coordinate \( \text{Si, Ge, Sn and Pb} \), John Wiley & Sons, Ltd: 2010; pp 139-197.


Chapter 3 Oxidation and related reactivity of cyclic (alkyl)(amino)germylene with N₂O, S₈ and TEMPO

3.1 Introduction

Ketone is a very important compound with the structure of R₂C=O, and has high application value in both industry and biology.¹ ³ It usually exists in monomeric forms rather than dimeric, oligomeric or polymeric forms. As a germanium analog of ketone, germanone has a more polarized Ge=O bond than that of ketone, so germanone generally exists as oligomeric or polymeric forms.⁴

The first monomeric germanone I was isolated by Tamao and co-workers in 2012,⁵ which was stabilized by the introduction of bulk groups (Figure 3.1). It is well known that the Ge=O double bond of germanone is weak, and its bond dissociation energy (108 kcal mol⁻¹) is obviously lower than that (172 kcal mol⁻¹) of the C=O double bond of ketone.⁴ Germanone favored to dimerize or oligomerize, because the germannium atom lack of the effective sp-hybridization due to its radial extensions.⁶-⁹

![Figure 3.1 Synthesis of germanone I.](image)

3.1.1 Intramolecular base stabilization of germanthione

The first stable heavy germanthione (R₂Ge=S) II with a terminal sulfur atom was reported by Veith and co-workers in 1989, which is stabilized by the coordination of intramolecular amine...
Meanwhile, the reaction of germylene III with oxygen gave the dimer IV instead of germanone V (Figure 3.2).4, 10, 13 Meanwhile, the reaction of germylene III with oxygen gave the dimer IV instead of germanone V (Figure 3.2), which is probably due to the higher bond polarity of Ge=O (1.44) than that of Ge=S (0.86). The bond polarity is a concept to describe the sharing of electrons between atoms within a covalent bond, in which the electron pairs shared between two atoms are not shared equally.

![Figure 3.2 Reaction of germylene III with S8 and O2.](image)

The second isolable germanthione VII stabilized by the intramolecular coordination of nitrogen atoms was reported by Parkin and co-workers in 1994 (Figure 3.3), where the stability of VII was also contributed from the coordination between nitrogen lone pair of electrons and d-orbital of germanium atom. To date, there are still not such germanones stabilized by the intramolecular coordination.14
Germanthiones II and VII were stabilized by the intramolecular donors that can donate the lone pair of electrons into the vacant $d$-orbital of germanium atom increasing its electron density and decreasing the net atomic charges of germainium. The intramolecular donors incidentally decrease the polarity of Ge=X double bonds as well to enhance the stability of germanthiones II and VII.  

3.1.2 Intermolecular base stabilization of germanone

The germanones and germanthiones stabilized intermolecularly by base also have been reported. Driess and co-workers reported the reactions of silylene/germylene DMAP/NHC adducts with N$_2$O to afford silanone and germanone adducts, respectively (Figure 3.4). This synthetic strategy has been first applied for the preparation of silanone adducts. (Figure 3.4) As the result, the nucleophilicity of germylene has been increased by the donors. In contrast to the free germlylene VIII, VIII cannot react with nitrous oxide at all.  

![Figure 3.3 Reaction of germlylene VI with S$_8$/PMe$_3$.](image1.png)

**Figure 3.3** Reaction of germlylene VI with S$_8$/PMe$_3$.

![Figure 3.4 Reaction of germlylene or silylene VIII with N$_2$O.](image2.png)

**Figure 3.4** Reaction of germlylene or silylene VIII with N$_2$O.
3.1.3 Steric-stabilization of germanone and germanthione

As mentioned in the introduction of Chapter 3.1, the first transient germanones was reported in 1971 by Satgé and co-workers,\(^2^4\) whereas the isolable monomeric germanone was reported in 2012.\(^5\) Two decades ago, its sulfur congeners, germanthione without inter- or intramolecular coordination of donors were isolated and characterized by Okazaki and co-workers (Figure 3.5).\(^2^5\)

![Figure 3.5 Reaction of tetrathiagermolane X with triphenylphosphine.](image)

It should be noted that when mesityl (Mes) group was employed instead of Tip group, a dimer of germanthione XI was formed indicating that Mes is not bulky enough to stabilize the reactive germanthione XI.\(^2^6\)-\(^2^7\)

Nagendran and co-workers reported a new germanone intramolecularly stabilized by both donor and acceptor sites.\(^2^8\) Interestingly, when they employed the μ-oxo dimer XIII instead of germylene XII, the addition of Lewis acids to XIII afforded the Lewis acids-germanone adducts XIV in a high yield. They also investigate the reactivity of germylene ZnCl\(_2\) adduct XV with N\(_2\)O, from which the same product XIV was obtained in 96% yield (Figure 3.6).
Although a few isolable germanones and germanthiones have been reported, more dimers or oligomers of germanones and germanthiones have been synthesized due to the deficiency of steric hindrance and/or the high polarity of Ge=X (X = O or S) double bonds.\textsuperscript{6-7,28}

### 3.2 Results and Discussions

As has been mentioned in chapter 2, we have synthesized cyclic (alkyl)(amino) germylene 1 which possesses a high-lying HOMO and low-lying LUMO, as well as bulky substituents to protect germanium center. Herein, we present oxidation reactions toward S\textsubscript{8}, N\textsubscript{2}O and TEMPO.

#### 3.2.1 Reaction of germylene 1 with S\textsubscript{8}

At first, we tested the reaction of germylene 1 with excess S\textsubscript{8}. The corresponding dimers 2\textsubscript{a} and 2\textsubscript{b} were obtained as a mixture of two diastereomers instead of the monomer. We carried out the optimization of the condition. Finally, the reaction gave the highest yield of 59\% under the 8:1 ratio of 1 and S\textsubscript{8} at ambient temperature. (Scheme 3.1).
**Scheme 3.1** Reaction of germylene 1 with $S_8$.

Remarkably, the products 2a and 2b have great thermodynamics stability, and they even can be purified by column chromatography under air atmosphere. Subsequently, X-ray crystallographic analysis (Figure 3.7) confirmed that the structure of the major product 2a possesses two 2,6-diisopropylphenyl groups located on the same side of the Ge$_2$S$_2$ plane. Both 2a and 2b involve a planar Ge$_2$S$_2$ four-membered ring. The S–Ge–S and Ge–S–Ge bond angles are 93.47(5)° and 86.56(5)° for 2a, and 94.01(12)° and 85.99(12)° for 2b, respectively. The Ge–S bond distances [2a: 2.2462(13) Å and 2.2406(13) Å, 2b: 2.231(3) Å and 2.237(3) Å] are in the range reported of Ge–S single bonds (2.17–2.25 Å),$^{29}$ and longer than the Ge=S double bond length of 2.049(3) Å in [Tb(Trip)Ge=S] (Tb = 2,4,6-(Me$_3$Si)$_2$CH)$_3$C$_6$H$_2$, Trip = 2,4,6-$^3$Pr$_3$C$_6$H$_2$).$^{25}$
Figure 3.7 Solid-state structures of 2a (left) and 2b (right). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: 2a) Ge1-S1 2.2462(13), Ge1-S2 2.2406(13), Ge2-S1 2.2356(13), Ge2-S2 2.2483(13); S2-Ge1-S1 93.47(5), S1-Ge2-S2 93.55(5). 2b) Ge1-S1 2.248(3), Ge1-S1 2.247(4); S1-Ge1-S1 94.27(12).

As mentioned in Chapter 3.1, when germantiones can be isolated, that should be stable enough through the protections of thermodynamic and kinetic factors. To get the isolable germantione, we introduced both intermolecular donors [pyridine, Me₃N, Ph₃P, and Et₃N] and acceptors [AlCl₃, GaCl₃, BPh₃ and B(C₆F₅)₃] to the mixture of 1 and S₈ (0.25 eq.). However, only the dimers 2 were obtained.²⁸,²⁹,³⁰-³¹

According to the ¹H NMR spectra, AlCl₃ and B(C₆F₅)₃ strongly interact with 1 over GaCl₃ (Figure 3.8). In the ¹H NMR spectra, a doublet for CH of 1 appears at 6.09 ppm, while the doublet was observed at 5.69 ppm with B(C₆F₅)₃, 5.82 ppm with AlCl₃, 6.06 ppm with GaCl₃, respectively (Figure 3.8).
Figure 3.8 Comparison of the \( ^1 \text{H} \) NMR spectra of germylene 1 and its Lewis acid adducts.

An unexpected product 3 was obtained from the reaction of 1 with GaCl\(_3\) (Scheme 3.2). 3' is a new germylene adduct which was stabilized by the imine N atom intramolecularly. The reaction of germylene 1 with HCl was hypothesized to generate intermediate 3', where HCl was generated from the hydrolysis of GaCl\(_3\) possibly. The single crystal of 3 was obtained by recrystallization and its solid-state structure was confirmed by X-ray crystallographic analysis (Figure 3.9).
Scheme 3.2 Generation of germylene 3.

Figure 3.9 Solid-state structure of 3. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ga1-Ge1 2.4857(5), Ge1-C1 1.969(3), Ge1-N1 1.988(3), Ge1-Cl1 2.1997(8), C3-N1 1.280(4), C1-C2 1.565(4), C2-C3 1.488(4); C1-Ge1-Ga1 133.64(9), C1-Ge1-N1 89.53(12), C3-N1-Ge1 110.7(2), C3-C2-C1 113.4(3), C2-C1-Ge1 104.2(2), N1-C3-C2 120.6(3).

The GeNC₃ five-membered ring of 3 are coplanar (the sum of internal pentagon angles = 538.43 ° for 3). The Ge1–N1 bond [1.988(3) Å] distance is slightly longer than that [Ge1–N1 1.859(11) Å] of 1 (Figure 2.18), indicating a property of dative bond rather than a covalent bond. The N1–C3 bond [1.280(4) Å] distances are slightly shorter than that C13–N1 [1.410(16) Å] of 1. The N1–Ge1–C1 bond angle [89.53(12) °] in 4 is more obtuse than the N1–Ge1–C15 bond angle of 86.5(5) ° in 1.
3.2.2 Reaction of germylene 1 with N$_2$O

Next we investigated the reaction of 1 with nitrous oxide that is well known as a powerful oxidizer for transition metals complexes and low-valent main group compounds.\(^{18-19, 28, 32-36}\) As mentioned in the introduction of chapter 3.1, Driess and co-workers reported the reactivity of germylene VIII toward N$_2$O; however, there was no reaction in the absence of the donors.\(^{18-19}\)

We carried out the reaction of germylene 1 with N$_2$O. After 1 hour at 40 °C, 1,3-digemadioxetane 4, the dimeric form of germanone 4', was obtained in 90% yield (Scheme 3.3). 4 was purified by recrystallization as a white solid, and the solid-state structure was confirmed by X-ray crystallographic analysis (Figure 3.10).

\begin{center}
\begin{tikzpicture}
  \node (A) at (0,0) {\(\text{Ar}\) \(\text{Ge}^+\) \(\text{Me}_3\text{Si}\) \(\text{SiMe}_3\)};
  \node (B) at (1,0) {\(\text{N}_2\text{O}\)};
  \node (C) at (2,0) {\(\text{C}_6\text{D}_6, 40 \, ^\circ\text{C}\)};
  \node (D) at (3,0) {\(\text{Ar}\) \(\text{Ge}=\text{O}\) \(\text{Me}_3\text{Si}\) \(\text{SiMe}_3\)};
  \node (E) at (4,0) {\text{Dimerization}};
  \node (F) at (5,0) {\(\text{Ar}\) \(\text{Ge}^\ldots\text{O}\ldots\text{Ge}\) \(\text{Ar}\)};
  \node (G) at (5,1) {\(\text{Me}_2\text{Si}\) \(\text{SiMe}_3\)};
  \node (H) at (5,0) {\(\text{Me}_3\text{Si}\) \(\text{SiMe}_3\)};

  \draw[->] (A) -- (B);
  \draw[->] (B) -- (C);
  \draw[->] (C) -- (D);
  \draw[->] (D) -- (E);
  \draw[->] (E) -- (F);
  \draw[->] (F) -- (G);
  \draw[->] (F) -- (H);
\end{tikzpicture}
\end{center}

\textit{Scheme 3.3} Reaction of germylene 1 with N$_2$O.

Product 4 displays a spiro-structure involving a nearly planar Ge$_2$O$_2$ four-membered ring in which two 2,6-diisopropylphenyl groups are located on the opposite side with respect to the Ge$_2$O$_2$ plane. The O–Ge–O and Ge–O–Ge bond angles are 86.35(8) ° and 93.65(8) °, respectively. The Ge–O bond distances [1.8084(16) Å and 1.8090(17) Å] are almost identical to those [1.821(2) Å and 1.822(2) Å] in digermadioxetane reported by Kira \textit{et al.}\(^{37-38}\)
Next, we also introduced the intermolecular Lewis bases [pyridine, Me$_3$N, Ph$_3$P, and Et$_3$N] and Lewis acids [AlCl$_3$, GaCl$_3$, Ph$_3$B and B(C$_6$F$_5$_)$_3$] to lower the polar of Ge=O double bond in the trapping reaction of the germanone 4', which afforded 4 as the final product. To compare the bond lengths of Ge–O in 4 with that of Ge–S bond in 3, we can find that Ge–O bond distances [1.8084(16) Å and 1.8090(17) Å] are strikingly shorter than Ge–S bond distances [2.2462(13) Å and 2.2406 Å]. Based on that, I think the stereoselectivity of the product 4 is depend on the steric effect, where the (Z) isomer is less stability than (E)-isomer.

3.2.3 Reaction of germylene 1 with TEMPO

2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) is a well-known stable radical reagent used in oxidation reactions. Kira and co-workers reported the reactions of TEMPO and metallylenes XVI (Scheme 3.4a), which prompted us to explore the reaction of TEMPO with germylene 1. We implemented the reaction of germylene 1 with two equivalents of TEMPO at ambient temperature, which afforded 5 in 71% yield (Scheme 3.4b). We also investigated 1:1 reaction
between 1 and TEMPO, which gave 5 again, and un-reacted 1 was recovered after the reaction. The thermolysis of 5 in benzene led to a complex mixture.

Scheme 3.4 The reaction of metallylenes with TEMPO.

The molecular structure of 5 was determined by X-ray crystallography in Figure 3.11. The Ge–O bond distances [1.814(3) Å and 1.796(3) Å] in 5 are lengthened with respect to the Ge=O double bond distance of 1.6468(5) Å in (Eind)₂Ge=O (Eind = 1,1,3,3,5,7,7-octaethyl-s-hydrindacen-4-yl group), and comparable to those [1.824(2) Å and 1.826(2) Å] in its homolog XVII.
Figure 3.11 Solid-state structure of 5. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ge1-O2 1.814(3), Ge1-O1 1.796(3), N2-O1 1.479(4), N3-O2 1.479(4), Ge1-N1 1.871(3), C15-Ge1 2.020(4); O1-Ge1-O2 104.32(13), N1-Ge1-C15 92.67(16).

3.3 Conclusion

In this chapter, we have investigated the reactivity of germylene 1 with S₈ and N₂O with and without Lewis acids. The oxidation reaction of 1 by S₈ led to the formation of the sulfido-bridged dimers 3 as a mixture of two diastereomers involving Ge₂S₂ four-membered ring framework. In contrast, when 1 was oxidized by N₂O, and only trans product containing the Ge₂O₂ four-membered ring skeleton was obtained. The reaction of 1 with TEMPO led to the formation of a 1:2 adduct 5.
3.4 Experimental Section

3.4.1 General Information

All reactions were performed under an atmosphere of argon by using standard Schlenk or dry box techniques; solvents were dried over sodium metal, potassium metal or CaH₂. All the substrates were obtained from the commercial sources or synthesized following literature procedures. Analytical thin layer chromatography was performed on triethylamine deactivated 0.25 mm silica gel 60-F254. Visualization was carried out with UV light. ¹H, and ¹³C spectra were obtained with AVIII 400MHz BBFO1 spectrometer at 298 K. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Coupling constants J are given in Hz. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with an OpticMelt Stanford Research System.

3.4.2 Reaction of germylene 1 with S₈

Cyclooctasulfur (S₈) (0.03 mmol, 7.4 mg) and 1 (0.23 mmol, 100 mg) were mixed in benzene (2 mL) and stirred for 1 hour at room temperature. After the solvent was removed under vacuum, the product was purified by silicone gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford colorless crystals of 2a (56 mg, 52%) and 2b (7.5 mg, 7%).

2a: Mp: 230 °C (dec); ¹H NMR (400 MHz, CDCl₃) δ 7.10 (t, J = 7.7 Hz, 2H, Ar-H), 6.89 (d, J = 7.7 Hz, 4H, Ar-H), 6.19 (d, J = 6.1 Hz, 2H, CH₃), 4.75 (d, J = 6.1 Hz, 2H, CH₃), 3.00 (dt, J = 13.6, 6.8 Hz, 4H, CH₃), 0.96 (d, J = 6.9 Hz, 12H, CH₃), 0.93 (d, J = 6.7 Hz, 12H, CH₃), 0.27 (s, 36H, Si(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ 146.96 (CQu), 140.92 (CH), 139.61 (CQu), 126.38 (CH), 123.58 (CH), 98.98 (CH), 28.18 (CH), 26.00 (CH₃), 22.91 (CH₃), 1.05 (Si(CH₃)₃); HRMS (ESI): m/z calcd for C₄₂H₇₂N₂S₈Si₄Ge₄: 931.2872. [(M+H)]⁺; found: 931.2892.

68
2b: Mp: 237 °C (dec); \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.18 (m, 6H, Ar-H), 6.32 (d, \(J = 6.0\) Hz, 2H, CH), 4.68 (d, \(J = 6.0\) Hz, 2H, CH), 3.24 (dt, \(J = 13.5, 6.8\) Hz, 4H, CH), 1.32 (d, \(J = 6.8\) Hz, 12H, CH\(_3\)), 1.04 (d, \(J = 6.8\) Hz, 12H, CH\(_3\)), −0.01 (s, 36H, Si(CH\(_3\))\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 147.88 (C\(_q\)), 140.31 (CH), 139.73 (C\(^\circ\)), 126.90 (CH), 123.67 (CH), 98.65 (CH), 28.55 (CH), 26.56 (CH\(_3\)), 22.27 (CH\(_3\)), 0.61 (Si(CH\(_3\))\(_3\)); HRMS (ESI): m/z calcd for C\(_{42}\)H\(_{75}\)N\(_2\)S\(_2\)Si\(_4\)Ge\(_2\) : \(931.2872\). \([(M+H)]^+\); found: 931.2898.

3.4.3 Reaction of germylene 1 with gallium trichloride

Gallium trichloride (0.23 mmol, 41 mg) and 1 (0.23 mmol, 100 mg) were mixed in benzene (2 mL) and stirred for 5 min at room temperature. After the solvent was removed under vacuum, the mixture was washed with hexane and then recrystallized with benzene to afford colorless crystal of 3 (47 mg, 31%). \(^1^H\) NMR spectrum is very broad (Figure 3.16), which cannot be determined.

3.4.4 Reaction of germylene 1 with nitrous oxide

Nitrous oxide (0.23 mmol, 10 mg) was carefully condensed at liquid nitrogen in benzene solution of 1 (0.23 mmol, 100 mg). The reaction mixture was heated and stirred at 40 °C for 1 hour. After the solvent was removed under vacuum, the product was purified by recrystallization to afford colorless crystal of 4 (93 mg, 90%). Mp: 278 °C (dec). \(^1^H\) NMR (400 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.19 (m, 2H, Ar-H), 7.15 – 7.11 (m, 4H, Ar-H), 6.34 (d, \(J = 6.3\) Hz, 2H, CH), 4.65 (d, \(J = 6.3\) Hz, 2H, CH), 3.50 (dt, \(J = 13.6, 6.8\) Hz, 4H, CH), 1.42 (d, \(J = 6.8\) Hz, 12H, CH\(_3\)), 1.21 (d, \(J = 6.8\) Hz, 12H, CH\(_3\)), 0.05 (s, 36H, Si(CH\(_3\))\(_3\)); \(^{13}\)C NMR (100 MHz, C\(_6\)D\(_6\)) \(\delta\) 147.81 (C\(^\circ\)), 141.12 (CH), 140.44 (C\(^\circ\)), 123.91 (CH), 120.00 (CH), 97.48 (CH), 28.23 (CH), 26.01 (CH\(_3\)), 22.70 (CH\(_3\)), 0.25 (Si(CH\(_3\))\(_3\)); HRMS (ESI): m/z calcd for C\(_{42}\)H\(_{75}\)N\(_2\)O\(_2\)Si\(_4\)Ge\(_2\) : 899.3329. \([(M+H)]^+\); found: 899.3361.
3.4.5 Reaction of germylene 1 with TEMPO

TEMPO (0.50 mmol, 78 mg) and 1 (0.23 mmol, 100 mg) were mixed in benzene (2 mL) and stirred for 5 min at room temperature. After the solvent was removed under vacuum, the product was recrystallized from hexane to afford colorless crystal of 5 (120 mg, 71%). Mp: 195 °C. $^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.18 (s, 3H, Ar-H), 6.43 (d, $J = 6.6$ Hz, 1H, CH), 4.66 (d, $J = 6.6$ Hz, 1H, CH), 3.87 (s, 2H, CH), 2.15 – 0.87 (m, 48H), 0.47 (s, 18H, Si(CH$_3$)$_3$); $^{13}$C NMR (100 MHz, C$_6$D$_6$) δ 147.32 (C$^q$), 144.21 (C$^q$), 140.67 (CH), 126.43 (CH), 123.63 (CH), 97.13 (CH), 61.35 (C$^q$), 61.15 (C$^q$), 41.85 (CH$_3$), 41.35 (CH$_3$), 34.30 (CH$_2$), 28.10 (CH$_2$), 26.47 (CH), 21.83 (CH$_2$), 16.96 (CH$_3$), 4.16 (Si(CH$_3$)$_3$); HRMS (ESI): m/z calcd for C$_{39}$H$_{74}$N$_3$O$_2$Si$_2$Ge: 746.4531. [(M+H)$^+$]; found: 746.4509.
3.4.6 $^1$H and $^{13}$C NMR Spectra

Figure 3.12 $^1$H NMR spectrum of 2a.

Figure 3.13 $^{13}$C NMR spectrum of 2a.
Figure 3.14 $^1$H NMR spectrum of 2b.

Figure 3.15 $^{13}$C NMR spectrum of 2b.
Figure 3.16 $^1$H NMR spectrum of 3.

Figure 3.17 $^1$H NMR spectrum of 4.
**Figure 3.18** $^{13}$C NMR spectrum of 4.

**Figure 3.19** $^1$H NMR spectrum of 5.
Figure 3.20 $^{13}$C NMR spectrum of 5.
3.5 Reference


Chapter 4 Equilibrium of silylium exchange: germylene activation of hydrosilanes under $B(C_6F_5)_3$ catalysis

4.1 Introduction

Hydrosilanes, which are organosilanes containing both organic substituents and at least one silicon–hydrogen bond, were utilized as the hydrogen source to reduce organic compounds, such as alcohol,\(^1\) ether,\(^3,5\) and ketone.\(^6-11\) Although the H atom in hydrosilanes exhibits certain hydridic nature due to the difference in electronegativity between Si ($\chi = 1.9$) and H ($\chi = 2.1$), they are not intrinsic nucleophiles. In general, hydrosilanes do not react spontaneously with organic substrates unless the substrates are strong electrophiles. Alternatively, hydrosilanes can be activated with electrophiles or Lewis acids, such as carbocation (R\(_3\)C)$^+$, and tris(pentafluorophenyl)borane $B(C_6F_5)_3$.\(^3,12-13\)

The activation of hydrosilanes with Group 14 divalent species has attracted much attention due to the oxidation processes that occur at the metallylene center under mild conditions. These are also considered the challenge in the chemistry of Group 14 metallylenes.\(^14-15\)

4.1.1 Activating the Si–H bond in hydrosilanes by carbenes

For many years, it was hypothesized that only transition-metal centers were able to activate hydrosilanes due to the high bond dissociation energy of the Si–H bond (90 kcal/mol), which is comparable to that of the C–H bond (92 kcal/mol).\(^16-18\) In 2010, the first example of hydrosilane activation by cyclic (alkyl)(amino) carbenes (CAACs) \(\text{I}\) and \(N\)-heterocyclic carbene (NHC) \(\text{II}\) was reported by Bertrand et al.; the corresponding products \(\text{III}\) and \(\text{IV}\) were generated via the insertion of the Si–H bond at the carbene center (Scheme 4.1).\(^15\)
Scheme 4.1 Hydrosilane activation by CAACs I and NHC II.

In 2012, Radius and co-workers observed the ring expansion of the NHCs when hydrosilane was treated at a higher reaction temperature. This ring expansion involved the cleavage of a C–N bond in the NHCs II (Scheme 4.2).\(^1\) A proposed reaction pathway for the formation of V is shown in Scheme 4.3. First, carbenes II are inserted into the hydrosilane Si–H bond to afford product VI. The subsequent C–N bond cleavage of NHCs is concomitant with the formation of a Si–N bond that generates the zwitterionic intermediate VII. The final step may involve the migration of a hydrogen atom from the Si center to the adjacent C atom to provide Vb.

Scheme 4.2 Reaction of various NHCs II with hydrosilanes.
Scheme 4.3 Proposed reaction path for the formation of Vb.

In 2015, Bielawski et al. reported another Si–H bond activation by DAC VIII to form IX (Scheme 4.4). This reaction is similar to the hydrosilanes activation by CAACs I\textsuperscript{15} and NHCs II\textsuperscript{19}. Collectively, the initial step is the formation of carbene→hydrosilane (supervalent) complexes, which has been considered the key step in the aforementioned Si–H bond activations.\textsuperscript{21}

Scheme 4.4 Reactions of DAC VIII with hydrosilanes.

4.1.2 Activating the Si–H bond in hydrosilanes by silylenes

Hydrosilanes activation by silylenes, the silicon analogues of carbenes, has also been reported. In 2003, Kira and co-workers showed that the reactions of silylene XI with various chlorosilanes afforded either the Si–H insertion X or Si–Cl bond insertion XII products (Scheme 4.5).\textsuperscript{22} The corresponding Si–H bond insertion products X were obtained exclusively, when the reactions of silylene XI with dimethylchlorosilane and trimethylsilane were performed. These reactions indicated that the Si–Cl insertion was more sensitive to steric hindrance than Si–H insertion.
Most recently, a reversible activation of hydrosilane by silylene XIII was reported by Kato et al.\textsuperscript{14} Silylene XIII readily reacted with phenylsilane at ambient temperature to afford the corresponding Si–H bond insertion product XIV in 49\% isolated yield (Scheme 4.6). It is noteworthy that the XIII: XIV ratio was temperature dependent. The proportional decrease with increasing temperature indicated that the reaction involved an equilibrium process.

\begin{center}
\textbf{Scheme 4.6} Reversible insertion reaction of silylene XIII with hydrosilane.
\end{center}

\textit{4.1.3 Activating the Si–H bond in hydrosilane by germylene}

In 2015, Tobita and co-workers reported the activation of hydrosilane by cationic germylene XV that contained tungsten and NHC units.\textsuperscript{23} The reaction of germylene XV with hydrosilane at room temperature underwent the Si–H bond insertion to afford the product XVI (Scheme 4.7). Notably, XV regenerated to achieve equilibrium when a fluorobenzene solution of XVI was heated to 60 °C. Although this Si–H bond activation process is reversible, the decomposition of both XV and XVI was observed when the mixture was heated above 80 °C.

\begin{center}
\textbf{Scheme 4.7} Reversible activation of hydrosilane by cationic germylene.
\end{center}
Scheme 4.7 Reaction of cationic germylene XV with hydrosilane.

Kato et al. subsequently reported the activation of hydrosilane by germylene XVII/B(C₆F₅)₃ adduct XVIII, where germylene XVII was regarded as a donor component of frustrated Lewis pairs (FLPs). The adduct XVIII reacted with hydrosilane to provide cationic germylene XIX via the Si–H bond cleavage (Scheme 4.8). In contrast, the reaction of XVIII with phenylsilane afforded XX, which was likely formed by an initial Si–H bond activation from the P/B Lewis pair. This was followed by the insertion of germylene into the Si–H bond of another phenylsilane.
It is well known that B(C₆F₅)₃ can be utilized for hydrosilanes activation, and ion-like silylium of the type R₃Si⁺δ⁺Y⁻ XXI are key species for reducing various organic substrates.²⁵-²⁹

Hydrosilanes activation by B(C₆F₅)₃ is reversible. Although XXI are not free silylium ions, they can act like silylium ions (Scheme 4.9).³,²⁴-²⁵,³⁰-³³

\[
\text{XXI}
\]

**Scheme 4.9** Reversible activation of hydrosilanes by B(C₆F₅)₃.

Hydrosilane activation by germylene has been reported both by Tobita et al.²³ and Kato et al.²⁴ To the best of our knowledge, although the direct activation of hydrosilane by neutral...
isolable germylene is unknown, the activation of Et₂SiH was utilized by Baines and co-workers trapping the transient germylene and affording the insertion product of Si-H bond.³⁴ Because we synthesized a cyclic (alkyl)(amino) germylene 1 possessing the high-lying HOMO and low-lying LUMO, as described in Chapter 2, here we present the reaction of germylene 1 with hydrosilanes under mild conditions.
4.2 Results and Discussions

4.2.1 Reaction of germylene 1 with hydrosilanes

First, the reaction of diphenylsilane 2a with germylene 1 was examined at room temperature. No reaction was observed until the mixture was heated to 100 °C for three days (Scheme 4.10). Despite such harsh conditions and prolonged reaction time, only 30% conversion from germylene 1 to an indeterminate symmetric product 3 was observed as determined by $^1$H NMR spectroscopy. The activation of triethylsilane (Et₃SiH) by germylene 1 was also investigated under the same conditions, but no reaction was observed.

Scheme 4.10 Activation of silane 2 with germylene 1.

As introduced in Chapter 4.1.3, B(C₆F₅)₃ can be utilized for hydrosilane activation. Herein, it is expected that B(C₆F₅)₃ can promote hydrosilane activation by 1. Hence, 20 mol% B(C₆F₅)₃ was employed for the reaction of germylene 1 with 10 equivalents of diphenylsilane 2a. After 3 h at 90 °C, three products formed, including the indeterminate symmetric product 3 (Scheme 4.11). The other two products were assigned to germynes 4a and 5, respectively, based on $^1$H NMR spectroscopy. Three new doublet peaks appeared for one of the respective $C(sp^2)H$ proton in the five-membered ring at 6.67 ppm (5), 6.45 ppm (4a) and 6.37 ppm (3). There was a peak with a chemical shift of 4.19 ppm, which overlapped with the $C(sp^2)H$ proton in 3 and belonged to the Me₃Si-$H$ proton in 6 (Figure 4.1).
Scheme 4.11 Activating diphenylsilane 2a by germylene 1 in the presence of catalytic B(C₆F₅)₃.

Figure 4.1 ¹H NMR spectrum (fitted) of the 2a and 1 mixture after 3 h at 90 °C.

The reaction of Et₃SiH 2b with germylene 1 in the presence of catalytic B(C₆F₅)₃ for 3 d at 100 °C produced similar results, and included indeterminate symmetric product 3 and germylene 4b via the unimolecular substitution reaction (Scheme 4.12).
Scheme 4.12 Activation of triethylsilane $2b$ with germylene $1$ in the presence of catalytic $B(C_6F_5)_3$.

The proposed mechanism for the formation of germylene $4$ is shown in Scheme 4.13. Two key equilibrium steps are involved in the reaction: a) the reaction of hydrosilane $2$ with $B(C_6F_5)_3$ is the initial step to afford silylium-like $2^\prime$, which further reacts with germylene $1$ to generate the intermediate $1a$; b) silylium $6^\prime$ reacts with $[HB(C_6F_5)_3]^\cdot$ to provide free $B(C_6F_5)_3$ and trimethylsilane $6$. Germylene $4$ is formed from $1a^\prime$ via a silyl [1,2] migration (Scheme 4.13).

Scheme 4.13 Proposed mechanism for the formation of products $4$.

Based on the proposed mechanism, it is hypothesized that an increase in the nucleophilicity of germylene $1$ will promote the reactivity of germylene $1$ by forming [germylene-SiR$_3$]$^\cdot$ adduct due to enhanced bond (Ge−Si) dissociation energy. Therefore, we modified the germylene $1$ by replacing the 2,6-diisopropylphenyl group with a stronger electron-donating inductive effect (+I) $1$-adamantyl group to increase the electron density at the germanium center.$^{35}$
First, we briefly analyzed the molecular orbitals (MOs) of germynes 1 and 7 using a DFT calculation at the theoretical B3LYP/6-31G(d,p) level (Figure 4.2). The HOMO–1 of 7 corresponds to the lone pair of germynes, which is higher in energy than that of 1. The HOMO–LUMO gap (3.98 eV) of germylene 7 is slightly larger than that (3.94 eV) of 1. This short analysis indicated that the modified germylene 7 would exhibit a stronger nucleophilicity than germylene 1, which fit our expectations.

**Figure 4.2** a) MOs comparison between 1 and 7; b) Plots of LUMO (top), HOMO (middle), and HOMO–1 (bottom) of 7 at the B3LYP/6-31G(d,p) level (the hydrogen atoms are omitted for clarity).

### 4.2.2 Synthesis of modified germylene 7

As indicated in Chapter 2, the synthesis of modified cyclic (alkyl)(amino) germylene 7 is based on the synthetic route to germylene 1. First, the reaction of 3,3-bis(trimethylsilyl)acrylaldehyde with amantadine was conducted in toluene, from which α,β-unsaturated imine 8 was obtained in 65% isolated yield (Scheme 4.14). The solid-state molecular structure of α,β-unsaturated imine 8 was determined by single-crystal X-ray diffraction analysis.
(Figure 4.3b). Then α,β-unsaturated imine 8 was reacted with 1.2 equivalents of germanium dichloride–dioxane complex to afford a dichlorogermane 9.

Scheme 4.14 Synthesis of α,β-unsaturated imine 8 and dichlorogermane 9.
Figure 4.3 Solid state structures of 7 (left) and 8 (right). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: a) N1-C11 1.365(5), C11-C12 1.332(6), C12-C13 1.517(5), Ge1-C13 2.002(4), Ge1-N1 1.859(3); N1-C11-C12 121.8, N1-Ge1-C13 87.07(15), C11-N1-Ge1 113.5(3), Ge1-C13-C12 104.7(3), Si1-C13-Si2 119.9(2); b) N1-C11 1.276(2), C11-C12 1.465(2), C12-C13 1.356(2); N1-C11-C12 119.5(14), C11-C12-C13 126.74(14).

The reaction of 9 with 2.5 equivalents of potassium graphite (KC8) was performed at −30 °C in THF for 20 h. Germylene 7 was isolated as a yellow solid in 93% yield after purification (Scheme 4.15). The solid-state structure of germylene 7 was determined by single-crystal X-ray diffraction analysis, it showed similar metric parameters to those of germylene 1 (Figure 4.3a).36

Scheme 4.15 Synthesis of germylene 7.
In the $^1$H NMR spectrum of 7, a singlet for Me$_3$Si group appears at 0.18 ppm, which is nearly identical to that (0.21 ppm) of germylene 1. Two doublets appear at 7.65 ppm and 6.22 ppm corresponding to the C(sp$^3$)-H protons in germylene 7, which are significantly shifted downfield compared with the corresponding peaks of germylene 1, 7.22 ppm and 6.09 ppm (Figure 4.4).

![Figure 4.4 $^1$H NMR spectra of germylene 1 (top) and germylene 7 (bottom).](image)

4.2.3 Reaction of germylene 7 with hydrosilanes in the presence of B(C$_6$F$_5$)$_3$

The reaction of 7 with hydrosilanes 2 in the presence of 20 mol% B(C$_6$F$_5$)$_3$ was examined. Different products were obtained depending on the hydrosilane substrates. When four equivalents of diphenylsilane 2a were used in the reaction, the corresponding germylene product 10 was obtained in 91% isolated yield (Scheme 4.16). Germylene 10 was characterized using $^1$H NMR spectroscopy (Figure 4.5) and single-crystal X-ray diffraction analysis (Figure 4.6). In comparison with 7, the Si1-C3-Si2 bond angle of 113.20(16) $^\circ$ in 10 is more acute than the Si1-C13-Si2 bond angle [119.3(2) $^\circ$] in 7. It is noteworthy that only 10 was observed in this reaction, germylene 11 with one SiMe$_3$ group and one SiPh$_2$H group was not observed.
Scheme 4.16 Reaction of germylene 7 with diphenylsilane 2a.

According to the $^1$H NMR spectrum of 10 (Figure 4.5), compound 10 does not possess the Me$_3$Si group because there are no peaks around 0.2 ppm. The $^1$H NMR spectra also showed same chemical shifts of two C($sp^2$)-H protons: First, one doublet peak appeared at 7.65 ppm for germylene 7, which was slightly shifted to high-field at 7.53 ppm for germylene 10. Second, another doublet peak appeared at 6.22 ppm for 7, but the corresponding peak was significantly shifted down-field at 6.66 ppm for 10 (Figure 4.5).
**Figure 4.6** Solid state structures of 10. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: N1-Ge1 1.862(3), N1-C1 1.385(4), C1-C2 1.371(5), C2-C3 1.462(5), C3-Ge1 2.036, C3-Si1 1.880(4), C3-Si2 1.880(4); N1-Ge1-C3 85.52(12), N1-C1-C2 116.4(3), C1-C2-C3 116.9(3), C2-C3-Ge1 106.2(2), Ge1-N1-C1 115.0(2), Si1-C3-Si2 113.20(16).

The reactions of germylene 7 with Et₃SiH 2b, PhSiH₃ 2c and Ph₃SiH 2d were also conducted in the presence of B(C₆F₅)₃ to afford germylenes 11 (Scheme 4.17). The reaction of germylene 7 with 4 equivalents of Et₃SiH 2b was performed in the presence of 20 mol% B(C₆F₅)₃ catalyst, the mixture was heated at 50 °C for 7 h to reach equilibrium (Figure 4.7 (middle)). Based on the proposed mechanism in Scheme 4.12, when the reaction of germylene 7 with 2b attained equilibrium, the removal of Me₃SiH 6 was performed to promote the equilibrium and the generation of product 11b (Figure 4.7 (bottom)).

**Scheme 4.17** Reactions of germylene 7 with various hydrosilanes 2.
Figure 4.7 $^1$H NMR spectra (fitted) for the reaction of germylene 7 with Et$_3$SiH for various times (2 h (top), 7 h (middle) and 30 h (bottom)).

When phenylsilane 2c was reacted with germylene 7 as well as 20 mol% B(C$_6$F$_5$)$_3$ at ambient temperature, the corresponding germylene 11c was also afforded in high yield. The products 11b and 11c were determined by $^1$H NMR spectroscopy. Attempts to obtain single crystals of 11b and 11c failed.

In the $^1$H NMR spectrum of germylene 11c, the integral of the singlet for the SiMe$_3$ group at 0.22 ppm is half that of germylene 7, which implies that one SiMe$_3$ group has been replaced with the SiPhH$_2$ group. Two doublets appear at 5.12 ppm and 4.80 ppm belonging to the SiPhH$_2$ group (Figure 4.8). This evidence supports the formation of germylene 11c from the reaction.
Figure 4.8 $^1$H NMR spectrum of germylene 11c.

The reaction of germylene 7 with triphenylsilane 2d was performed at 120 °C. After 12 h, solvent and by-product Me$_3$SiH 6 were removed under vacuum. By repeating the same processes three times, 81% of germylene 7 was converted to germylene 11d. The reaction was monitored by $^1$H NMR spectroscopy, which showed that a doublet at 6.25 ppm and a singlet at 0.20 ppm for germylene 7 decreased gradually while the corresponding peaks at 6.55 ppm and 0.02 ppm for 11d increased concomitantly (Figure 4.9). Unfortunately, attempts to obtain a single crystal of 11d failed.
Figure 4.9 $^1$H NMR spectra for the reaction of germylene 7 with triphenylsilane 2d in the presence of B(C$_6$F$_5$)$_3$ for 12 h (top), 24 h (middle), and 36 h (bottom).

Although all attempts to obtain single crystals of 11 failed, the corresponding products 12 were afforded as yellow solids when the stoichiometry trapping reactions of germylene 11 with one equivalent of diphenyl diselenide were carried out at room temperature in benzene (scheme 4.18).$^{37-38}$ These products 12 were characterized using NMR spectroscopy and single-crystal X-ray diffraction analysis (Figure 4.10).

Scheme 4.18 Reactions of germylene 11 with diphenyl diselenide.
Figure 4.10 Solid state structures of 12b and 12d. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: 12b) C13-Ge1 1.981(5), Ge1-N1 1.858(4), Ge1-Se2 2.3663(7), Ge1-Se1 2.3897(7), C13-Si2 1.900(5), C13-Si1 1.919(5); Se2-Ge1-Se1 103.28(2), N1-Ge1-C13 92.31(19), Si2-C13-Si1 114.2(2); 12d) Ge1-N1 1.827(6), Ge1-Se1 2.3871(11), Ge1-Se2 2.3930(10), C1-Ge1 1.990(7), C1-Si2 1.896(8), C1-Si1 1.913(7), Si2-C1-Si1 114.2(4), N1-Ge1-C1 93.3(3), Se1-Ge1-Se2 107.54(4).

In comparison to the bond parameters of compounds 12b and 12d, the Ge1-Se1 bond length of 2.3663(7) Å in 12b is notably shorter than that of 2.3871(11) Å in 12d. Moreover, the C13-Si1 bond length of 1.919(5) Å in 12b is slightly longer than that of C1-Si1 1.913(7) in 12d. The Se1-Ge1-Se2 bond angle of 103.28(2)° in 12b is more acute than the Se1-Ge1-Se2 bond angle [107.54(4)°] in 12d. The difference might have resulted from the steric effect, where the Ph₃Si group is bulkier than the Et₃Si group.

4.2.4 Mechanism elucidation and kinetic studies

To verify the hypothesized mechanism (Scheme 4.13), the reaction of germylene 7 with 1 equivalent of B(C₆F₅)₃ was performed in C₆D₆ at room temperature, which afforded the corresponding adduct 12 (Scheme 4.19a). In the ¹H NMR spectrum, the doublets at 7.51 ppm
and 6.09 ppm for adduct 12 shifted compared with the corresponding peaks of germylene 7, 7.65 ppm and 6.23 ppm (Figure 4.11).

In the proposed mechanism, the formation of germylene 11 involved the intermediate 1a. The reaction of germylene 7 with Et3SiB(C6F5)4 was conducted in benzene at ambient temperature subsequently certifying the hypothesis (Scheme 4.19b). The reaction was monitored by 1H NMR spectroscopy, in which the formation of germylene 11b was observed. The proportion of 11b increased gradually and was 33% for 37 h (Figure 4.11).

Scheme 4.19 Reaction of germylene 7 with B(C6F5)3 or Et3SiB(C6F5)4.
Figure 4.11 $^1$H NMR spectra of the mixture of germylene 7 with B(C$_6$F$_5$)$_3$ or Et$_3$SiB(C$_6$F$_5$)$_4$.

When the reaction of germylene 7 with 1 equivalent of Et$_3$SiB(C$_6$F$_5$)$_4$ and 1 equivalent of NaHB(C$_6$F$_5$)$_3$ as the H$^-$ source was conducted, germylene 11b formed with a 41% after 36 h. The reaction was promoted by the addition of NaHB(C$_6$F$_5$)$_3$ (Scheme 4.20).

![Scheme 4.20](image)

Scheme 4.20 Reaction of germylene 7 with Et$_3$SiB(C$_6$F$_5$)$_4$ and NaHB(C$_6$F$_5$)$_3$.

To further elucidate the mechanism for the reaction of germylene 7 with hydrosilanes 2 in the presence of B(C$_6$F$_5$)$_3$, kinetic experiments were also conducted. First, the reactions of germylene 7 with excess Et$_3$SiH were plotted as a pseudo first-order reaction versus time (Figure 4.12) or a pseudo second-order reaction versus time at 333 K using the initial rate data (Figure 100).
4.13). The slope remains stationary when Et₃SiH are conducted more than 5 equivalents, but there is a low R-squared value for the first-order reaction equation, which indicates the pseudo reaction is second-order under these conditions.

Other kinetic studies were performed at various temperatures (323 K – 343 K), in which the reaction of germylene 7 with 1.7 equivalents of Et₃SiH in the presence of 20 mol% of B(C₆F₅)₃ were conducted (Table 4.1). The highest concentration of germylene 11b was determined at 323 K.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>323</th>
<th>333</th>
<th>343</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (M) of 11b</td>
<td>0.0319</td>
<td>0.0317</td>
<td>0.0292</td>
</tr>
</tbody>
</table>

*Table 4.1* Concentration of 11b at various temperatures, when the reaction reached equilibrium.

(Determined by ¹H NMR spectroscopy)
Figure 4.12 Pseudo-first order plots for the reaction of germylene 7 with various equivalents of Et₃SiH at 333 K.
Figure 4.13 Pseudo-second order plots for the reaction of germylene 7 with various equivalents of Et₃SiH at 333 K.
4.3 Conclusion

In conclusion, a modified germylene 7 with an adamantyl group on the N atom was developed. In the reaction of 7 with hydrosilanes in the presence of 20 mol% B(C₆F₅)₃, germylene 7 was transformed into germylenes 10 and 11 via silyl group exchange. Our mechanistic study suggests that the initial step is hydrosilane activation by B(C₆F₅)₃ to generate silylium ion which subsequently forms an adduct with germylene 7. Elimination of one silyl group on the \( sp^3 \)-carbon in the GeNC₃ five-membered ring would yield the cyclic germene intermediate 1b, from which germylenes 10 and 11 may be formed via a migration of the silyl group from the Ge atom to the adjacent C atom.
4.4 Experimental Section

4.4.1 General Information

All reactions were performed under an atmosphere of argon by using standard Schlenk or dry box techniques; solvents were dried over Na metal, K metal or CaH₂. All the substrates were obtained from the commercial sources or synthesized following literature procedures. ¹H, ¹³C and ²⁹Si spectra were obtained with AVIII 400 MHz BBFO1 and BBFO2 spectrometers at 298 K. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Coupling constants J are given in Hz. Electrospray ionization (ESI) mass spectrum was obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with an OpticMelt Stanford Research System.

4.4.2 Synthesis of imine 8

Amantadine (45 mmol, 6.81 g) and 3,3-bis(trimethylsilyl)acrylaldehyde (50 mmol, 10.00 g) were mixed in toluene (100 mL). The mixture was refluxed overnight. After cooling to room temperature, the product was purified by recrystallization in pentane to afford 8 as a white solid (12.9 g, 72%). Mp: 92 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, J = 9.1 Hz, 1H, CH), 7.16 (d, J = 9.1 Hz, 1H, CH), 2.16 (s, 3H, CH), 1.79 – 1.66 (m, 12H, CH₂), 0.26 (s, 9H, Si(CH₃)₃), 0.17 (s, 9H, Si(CH₃)₃); ¹³C NMR (101 MHz, CDCl₃) δ 157.01 (C), 152.42 (C), 57.84 (C), 43.17 (CH₂), 36.50 (CH₂), 29.53 (CH), 2.37 (Si(CH₃)₃), 0.10 (Si(CH₃)₃); HRMS (ESI): m/z calcd for C₁₉H₃₅NSi₂: 333.2308. [(M+H)⁺; found: 334.2392.

4.4.3 Synthesis of cyclic (alkyl)(amino) dichlorogermane 9

(E)-N-(adamantan-1-yl)-3,3-bis(trimethylsilyl)prop-2-en-1-imine 8 (4 mmol, 1.42 g) and dichlorogermadiyl dioxane (4 mmol, 0.93 g) were mixed in benzene (20 mL). The mixture was
stirred at room temperature overnight and then vacuumed to remove the solvent. The product 9 was obtained as a white solid (1.93 g, 96%). Mp: 134 °C; ¹H NMR (400 MHz, C₆D₆) δ 6.61 (d, J = 6.6 Hz, 1H, CH), 4.72 (s, 1H, CH), 1.94 (s, 6H, CH₂), 1.88 (s, 6H, CH₂), 1.45 (s, 6H, CH), 0.27 (s, 18H, Si(CH₃)₃); ¹³C NMR (101 MHz, C₆D₆) δ 132.08 (C), 98.46 (C), 55.81 (C), 43.75 (C₂H), 35.97 (C₂H), 29.82 (C), 0.46 (Si(CH₃)₃); HRMS (ESI): m/z calcd for C₁₉H₃₅Cl₂GeNSi₂: 477.0897. [(M+H)]⁺; found: 478.0979.

4.4.4 Synthesis of modified cyclic (alkyl)(amino) germylene 7

9 (2 mmol, 1.02 g) and KC₈ (6 mmol, 0.81 g) were mixed in benzene (30 mL). The mixture was stirred at 60 °C for 24 h. After stirring for another 30 min at room temperature, the mixture was filtered and concentrated under vacuum to afford product 7 as a light-yellow solid (0.78 g, 90%). Mp: 73 °C; ¹H NMR (400 MHz, C₆D₆) δ 7.65 (d, J = 3.6 Hz, 1H, CH), 6.22 (d, J = 3.5 Hz, 1H, CH), 2.00 (s, 9H, s), 1.55 (d, J = 4.1 Hz, 6H, CH₂), 0.18 (s, 18H, Si(CH₃)₃); ¹³C NMR (101 MHz, C₆D₆) δ 140.08 (C), 119.08 (C), 78.53 (C), 75.41 (C), 47.13 (C₂H), 36.24 (C₂H), 30.11 (C), 1.42 (Si(CH₃)₃); ²⁹Si NMR (79 MHz, C₆D₆) δ −8.32 (Si(CH₃)₃); HRMS (ESI): m/z calcd for C₁₉H₃₅GeNSi₂: 407.1520. [(M+H)]⁺; found: 408.1598.

4.4.5 Reactions of hydrosilanes 2 with germylene 7 in the presence of B(C₆F₅)₃

Germylene 7 (0.05 mmol, 20 mg) and hydrosilanes 2a (0.20 mmol, 37 mg) were mixed in C₆D₆ (0.5 mL) in the presence of B(C₆F₅)₃ (0.01 mmol, 5 mg), and the mixture was heated at 100 °C for 12 hours. After all volatiles were removed under vacuum, recrystallization in pentane afforded 10 as a light-yellow solid in 91% (29 mg). Mp: 129 °C; ¹H NMR (400 MHz, C₆D₆) δ 7.76 – 7.68 (m, 4H, Ar-H), 7.55 (dd, J = 7.8, 1.5 Hz, 4H, Ar-H), 7.53 (d, J = 4.3 Hz, 1H, CH), 7.13 (dt, J = 5.9, 3.4 Hz, 8H, Ar-H), 7.08 (dt, J = 13.8, 4.1 Hz, 4H, Ar-H), 6.65 (d, J = 4.3 Hz, 1H, CH), 5.64 (t, 2H, Ph₂Si-H), 1.90 (s, 3H, CH₃), 1.67 (d, J = 2.2 Hz, 6H, CH₂), 1.46 (dd, J = 29.3, 12.0 Hz, 6H, CH); ¹³C NMR (101 MHz, C₆D₆) δ 142.69 (CH), 135.21 (C), 135.14 (CH), 134.99 (CH), 129.50 (CH), 129.24 (CH), 127.68 (CH), 127.35 (CH), 116.84 (CH), 67.69 (C), 106.
57.10 (C\textsuperscript{9}), 46.49 (CH\textsubscript{2}), 36.08 (CH\textsubscript{2}), 29.95 (CH); \textsuperscript{29}Si NMR (79 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta\) –24.33 (d, \(J = 201.8\) Hz, SiPh\textsubscript{2}H); HRMS (ESI): m/z calcd for C\textsubscript{37}H\textsubscript{39}GeNSi\textsubscript{2}: 627.1833. [(M+H)]\textsuperscript{+}; found: 628.1895.

Germylene 7 (0.05 mmol, 20 mg) and hydrosilanes 2b (0.20 mmol, 24 mg) were mixed in C\textsubscript{6}D\textsubscript{6} (0.5 mL) in the presence of B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (0.01 mmol, 5 mg), and the mixture was heated at 60 °C for 5 hours. After the mixture was cooled to room temperature, all volatiles were removed under vacuum. Because the germylene 11b was failed to isolate, PhSeSePh (0.05 mmol, 16 mg) was added to a benzene (1 mL) solution of 11b. After stirring at ambient temperature for 30 minutes, the solvent was removed under vacuum to afford 12b. The product 12b as a light-yellow solid in 91% (31 mg). Mp: 102 °C (dec); \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta\) 7.89 – 7.72 (m, 2H, Ar-H), 7.50 – 7.35 (m, 2H, Ar-H), 7.07 – 6.99 (m, 3H, Ar-H), 6.92 (t, \(J = 6.8\) Hz, 3H, Ar-H), 6.61 (d, \(J = 6.2\) Hz, 1H, CH), 4.92 (d, \(J = 6.2\) Hz, 1H, CH), 1.87 (s, 3H, CH), 1.81 – 1.69 (m, 7H, CH\textsubscript{2}), 1.49 – 1.35 (m, 6H, CH\textsubscript{2}), 1.20 – 1.11 (m, 14H, CH), 0.46 (s, 9H, Si(CH\textsubscript{3})\textsubscript{3}); \textsuperscript{13}C NMR (101 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta\) 137.86 (C\textsubscript{9}), 137.12 (CH), 135.79 (CH), 133.75 (CH), 130.08 (C\textsuperscript{9}), 128.98 (C\textsuperscript{9}), 128.68 (CH), 128.61 (CH), 128.13 (CH), 126.55 (CH), 99.93 (CH), 55.58 (C\textsuperscript{9}), 43.81 (CH\textsubscript{2}), 36.18 (C\textsuperscript{9}), 32.24 (CH), 30.02 (CH), 8.73 (CH\textsubscript{3}), 6.47 (CH\textsubscript{2}), 1.92 (Si(CH\textsubscript{3})\textsubscript{3}); \textsuperscript{29}Si NMR (79 MHz, C\textsubscript{6}D\textsubscript{6}) \(\delta\) 5.28 (SiEt\textsubscript{3}), −0.87 (Si(CH\textsubscript{3})\textsubscript{3}); HRMS (ESI): m/z calcd for C\textsubscript{34}H\textsubscript{51}GeNSe\textsubscript{2}Si\textsubscript{2}: 763.1102. [(M+H)]\textsuperscript{+}; found: 764.1177.

Germylene 7 (0.05 mmol, 20 mg) and hydrosilanes 2c (0.20 mmol, 21 mg) were mixed in C\textsubscript{6}D\textsubscript{6} (0.5 mL) in the presence of B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (0.01 mmol, 5 mg), and the mixture was stirred at room temperature for 12 hours. Then the mixture was removed under vacuum. Because the germylene 11c was failed to isolate, PhSeSePh (0.05 mmol, 16 mg) was added to benzene (1 mL) solution of 11c. After stirring at room temperature for 30 minutes, the solvent was removed under vacuum to afford 13c as a light-yellow oil. HRMS (ESI): m/z calcd for C\textsubscript{34}H\textsubscript{43}GeNSe\textsubscript{2}Si\textsubscript{2}: 755.0476. [(M+H)]\textsuperscript{+}; found: 756.0436.
Germylene 7 (20 mg, 0.05 mmol) and hydrosilanes 2d (52 mg, 0.20 mmol) were mixed in 
C₆D₆ (0.5 mL) in the presence of B(C₆F₅)₃ (5 mg, 0.01 mmol) and the mixture was heated at 
120 °C for 12 hours. After the mixture was cooled to room temperature, the solvent was removed 
under vacuum. Because germylene 11d was failed to isolate, PhSeSePh (0.05 mmol, 16 mg) was 
added to benzene (1 mL) solution. After stirring at ambient temperature for 30 minutes, the 
solvent was removed under vacuum to afford 13d as a light-
Yellow solid in 94% (38 mg). Mp: 154 °C (dec); ¹H NMR (400 MHz, C₆D₆) δ 8.09 (s, 5H, CH), 7.91 – 7.82 (m, 2H, CH), 6.58 – 6.44 (m, 2H, CH), 5.38 (d, J = 6.2 Hz, 1H, CH), 1.86 – 1.82 (m, 3H, CH₂), 1.79 – 1.71 (m, 3H, CH₂), 1.60 – 1.53 (m, 3H, 
CH₂), 1.48 – 1.33 (m, 6H, CH), 0.23 (s, 9H, Si(CH₃)₃); ¹³C NMR (101 MHz, C₆D₆) δ 138.49, 138.00 (CH), 136.97 (CH), 134.73 (CH), 129.23 (CH), 128.93 (C⁰), 128.75 (C⁰), 128.58 (CH), 128.15 (CH), 127.29 (CH), 126.74 (CH), 99.91 (CH), 55.12 (C⁰), 43.67 (CH₂), 36.10 (CH₂), 30.00 (CH), 29.68 (C⁰), 1.71 (Si(CH₃)₃); ²⁹Si NMR (79 MHz, C₆D₆) δ −0.27 (Si(CH₃)₃), −14.43 
(SiPh₃); HRMS (ESI): m/z calcd for C₄₆H₅₁GeNSe₂Si₂: 907.1102. [(M+H)]⁺; found: 908.1219.

4.4.6 Kinetic studies

General method for pseudo-first order reactions: Germylene 7 (20 mg, 0.05 mmol), Et₃SiH 
2b (100 mg, 0.86 mmol; or 150 mg, 1.29 mmol), the internal standard p-xylene (2.65 mg, 0.025 
mmol) and C₆D₆ (0.5 mL) were loaded into a dried J. Young NMR tube and sealed. The reaction 
was heated at 333.15 K and monitored automatically by NMR spectroscopy with 5 minutes 
interval. Based on the integration of germylene 11b, which was plotted versus time following a 
pseudo-first order kinetic equation.

General procedures for the activation of Et₃SiH 2b by germylene 7 at various temperatures: 
Germylene 7 (20 mg, 0.05 mmol), Et₃SiH 2b (10 mg, 0.086 mmol), the internal standard p-
xylene (2.65 mg, 0.025 mmol) and C₆D₆ (0.5 mL) were loaded into a dried J. Young NMR tube 
in glovebox. The mixture was heated at a temperature range from 323.15 K to 343.15 K, which
was automatically monitored by NMR spectroscopy with 5 minutes interval. Based on the integration of germylene 11b, the logarithmic plot of the concentration of germylene 11b was plotted against time.
4.4.7 $^1$H, $^{13}$C, and $^{29}$Si NMR spectra

**Figure 4.14** $^1$H NMR spectrum of 8

**Figure 4.15** $^{13}$C NMR spectrum of 8
Figure 4.16 $^1$H NMR spectrum of 9

Figure 4.17 $^{13}$C NMR spectrum of 9
Figure 4.18 $^1$H NMR spectrum of 7

Figure 4.19 $^{13}$C NMR spectrum of 7
Figure 4.20 $^{29}$Si NMR spectrum of 7

Figure 4.21 $^1$H NMR spectrum of 10
Figure 4.22 ¹³C NMR spectrum of 10

Figure 4.23 ²⁹Si NMR spectrum of 10
Figure 4.24 $^1$H NMR spectrum of 12b

Figure 4.25 $^{13}$C NMR spectrum of 12b
Figure 4.26 $^{29}$Si NMR spectrum of 12b

Figure 4.27 $^1$H NMR spectrum of 12d
Figure 4.28 $^{13}$C NMR spectrum of 12d

Figure 4.29 $^{29}$Si NMR spectrum of 12d
4.5 Reference


Chapter 5 Reactions of germynes with metal complexes

5.1 Introduction

The existence of stable carbenes was first described by Fischer et al. in 1964 in the complex W(CO)₅(COCH₃)(CH₃).¹ Since this report, carbenes have become ubiquitous neutral ligands in coordination chemistry of transition metals.²⁻⁷

In this chapter, the various synthetic routes of dicarbene gold(I) complexes and their electronic properties have been summarized. The first dicarbene gold(I) complex I was synthesized by Burini and co-workers in 1989, by reacting C-imidazolyl lithium salts with chloro(triphenylphosphine)gold(I) (Scheme 5.1). The same method has been applied for the synthesis of the corresponding dicarbene silver(I) complexes.⁸

![Scheme 5.1 Synthesis of dicarbene gold(I) complexes I.](image)

The dicarbene gold(I) complexes have also been synthesized via carbene transfer from corresponding W or Cr carbene complexes.⁹⁻¹¹ In 1998, Liu and co-workers reported that the transfer reaction between the N-heterocyclic carbene (NHC) tungsten carbonyl complex II and (Me₂S)AuCl, led to the formation of di-NHC gold(I) complex III, which was obtained as a yellow liquid in 64% yield (Scheme 5.2).⁹
Following these reports in the literature, the chemistry of dicarbene gold(I) has been intensively studied both experimentally and theoretically. Conventionally, dicarbene gold(I) complexes are synthesized through the direct reaction of tetrahydrothiophene gold(I) chloride ((THT)AuCl) with two equivalents of NHCs or imidazolium salts. In 2006, Baker et al. reported the synthesis of di-NHC gold(I) complexes IV by the reaction of two equivalents of NHCs with (Me₂S)AuCl, wherein the NHCs were prepared in situ by the deprotonation of the imidazolium salt with lithium bis(trimethylsilyl)azanide (LiHMDS) at room temperature (Scheme 5.3).

The dicarbene gold(I) complexes can also be synthesized in a stepwise manner. In 2008, Bertrand and co-workers reported the formation of the dicyclic (alkyl)(amino) carbenes (CAACs) gold(I) complex IV. These CAACs, which feature bulky and rigid substituents at the carbon adjacent to the carbene center, reacted with one equivalent of (Me₂S)AuCl to afford the corresponding CAAC gold(I) chloride V. Alternatively, di-CAAC gold(I) complexes VI were
obtained when the CAACs containing the smaller and more flexible cyclohexyl or cyclohexylene groups were used as reactants (Scheme 5.4a). Complex VI could further react with lithium at room temperature in THF to afford electron rich the di-CAAC stabilized gold(0) complex (Scheme 5.4b).\textsuperscript{18}

\textbf{Scheme 5.4} a) Reactions of CAACs with (Me₂S)AuCl; b) reactions of complexes VI\textsubscript{d} with lithium to afford the gold(0) complex.

In addition to the above mentioned synthetic route, di-NHC gold(I) complex VII was synthesized by the reaction of 0.5 equivalents of (SMe₂)AuCl with the corresponding \textit{in situ} generated NHC Ag(I) complex (Scheme 5.5). This reaction was reported by Hong \textit{et al.} in 2013 and performed at ambient temperature in dichloromethane (DCM).\textsuperscript{19}
Scheme 5.5 Synthesis of dicarbene gold(I) complex VII.

Hetero-di-NHC gold(I) complexes containing two different NHCs have generally been synthesized by the reaction of mono NHC gold(I) complexes with one equivalent of a different free NHC or its precursor imidazolium salt. The first hetero-di-NHC gold(I) complex IX was reported by Raubenheimer and co-workers in 1995, where one equivalent of CF₃SO₃H was reacted with VIII to afford complex IX (Scheme 5.6).

Scheme 5.6 Synthesis of the first hetero-di-NHC gold(I) complex IX.

In 2013, Huynh and co-workers reported the synthesis of hetero-di-NHC gold(I) complexes XI, which involved the reaction of the NHC gold(I) acetate X with imidazolium salts (Scheme 5.7). Homo-di-NHC gold(I) complexes were formed when the reaction time was prolonged.
Scheme 5.7 Reactions of complex X with different imidazolium salts.

Moreover, the bonding and electronic properties of di-NHC gold(I) complexes have also been studied theoretically. Formally, the bonding in a di-NHC gold(I) complex involves both NHC:→Au(I)←:NHC σ-donation and NHC:←Au(I)→:NHC π-back-donation. However, NHCs are often considered as pure σ donors because the empty p orbital of carbene is filled by the π electrons from the nitrogen atom.23-28

In 2004, Frenking and co-workers reported a computational study on the π-interactions between Group 11 metals in the +1 oxidation state and NHC ligands.12 The energy decomposition analysis (EDA) clarified the contributions of σ and π orbital interactions (Figure 5.1).29-31 The out-of-plane π_⊥ back-donation was found to contribute about 20% to the total orbital interaction energies, and the in-of-plane of π_∥ back-donation accounted for 10% of the entire interaction energy.
Figure 5.1 The interactions between in-of-plane($\pi_\parallel$) and out-of-plane($\pi_\perp$).

In 2014, Zuccaccia et al. also reported their studies on the interactions between gold(I) and NHC ligands. Their calculations suggested that $\pi$ back-donation is a sensitive and tunable component of the $C_{\text{carbene}}$–Au bond. Moreover, the $\pi/\sigma$ contribution ratio can be modulated from more than half of $\sigma$-donation to pure $\sigma$-donation depending on the auxiliary ligand(L) of the [NHC–Au(I)–L] complex (Figure 5.2). The nature of bonding between the CAAC ligand and gold(I) metal in IV was also calculated by Frenking et al. These authors suggested that the CAAC ligands are stronger $\pi$-acceptors than $\sigma$-donors in IV, they prefer to accept the $d$ electrons of the gold(I) atom.

Figure 5.2 The two components of the Au–NHC bond in [NHC–Au–L] systems.

While di-NHC gold(I) complexes have been extensively studied, neither disilylenes nor digermylenes gold(I) complexes have been reported so far. As a relevant study, it has been reported that the reactions of Lewis base-stabilized germylenes with gold(I) halides furnishes germylene-gold(I) species. In 2012, Castel et al. reported that the reaction of phosphaalkenyl germylene XII with gold(I) halide complexes afforded the germylene gold(I) chloride complex XIII (Scheme 5.8a). Leung and co-workers reported the synthesis of the pyridine-coordinated germanium(II) gold(I) complex XV by the direct complexation reaction between germanium(II)
**Scheme 5.8** Complexation reactions of germynes with gold(I) halides.

Compounds containing Au–Ge σ bonds can be synthesized either via the insertion reaction of germynes into gold(I)–halide bonds,\(^\text{36-38}\) or by the displacement reaction of the R₃Ge⁻ anion with gold(I) halide species.\(^\text{39-40}\) The insertion reaction of GeCl₂·dioxane into the Au–Cl bond was first reported by Schmidbaur *et al.* in 1995 in the synthesis of the germanium-gold(I) complex **XVI** (Scheme 5.9a).\(^\text{38}\) Analogously, Sharp and co-workers reported that germylene **XVII** inserted into the Au–Cl bond of R₃PAuCl complexes to form germanium-gold(I) complexes **XVIII**(Cl) (Scheme 5.9b).\(^\text{41}\) Moreover, when the Cl⁻ of L→Au–Cl was replaced with the tetrafluoroborate (BF₄⁻) analogue in the preceding reaction, fluoride abstraction took place from the BF₄⁻ anion and the complex **XVIII**(F) was formed.
Scheme 5.9 Insertion reactions of germynes into the Au–Cl bond.

The displacement reaction of the R₃Ge⁻ anion with gold(I) chloride complexes was first reported by Gade and co-workers in 1996. In this study, the triamidometalate XIX was reacted with [R₄P][AuX₂] to afford the corresponding digermaaurates XX (Scheme 5.7).

\[
\begin{align*}
\text{a)} & \quad \text{Ph}_3\text{P} + \text{GeCl}_2 \cdot \text{dioxane} \xrightarrow{\text{THF}} \text{Ph}_3\text{P} \rightarrow \text{AuGeCl}_3 \\
\text{b)} & \quad \text{LAuCl} + \text{Me}_3\text{Si} \rightarrow \text{Me}_3\text{Si} \rightarrow \text{Ge} \rightarrow \text{Toluene r.t.} \quad \text{Me}_3\text{Si} \rightarrow \text{Ge} \rightarrow \text{AuL} \\
& \quad \text{Cl} (\text{F}) \quad \text{Me}_3\text{Si} \rightarrow \text{N} \quad \text{Me}_3\text{Si} \rightarrow \text{N} \quad \text{Cl} \\
& \quad \text{SiMe}_3 \quad \text{SiMe}_3 \\
& \quad \text{XVII} \quad \text{XVIII} \\
& \quad (L = \text{Ph}_3\text{P}, \text{Cy}_3\text{P}, \text{Ph}_2\text{MeP}, \text{PhMe}_2\text{P})
\end{align*}
\]

Scheme 5.10 Reactions of the triamidogermalithium XIV with gold(I) complexes.

Recently, Majumdar et al. have reported the preparation of the dicationic bis(germanium(II)) gold(I) complex XXI, in which the sequestered germanium(II) center was coordinated by an acyclic tetradeutate bis(α-iminopyridine) ligand (Scheme 5.11). The pentacationic gold(I) complex XXII shows a linear geometry with the Ge–Au–Ge bond angle of 166.538(16)°. All Ge–N bonds distances are shorter than that of dicationic germanium(II) XXI, which indicates an enhanced donation from the N atoms of both imines and pyridines to the cationic germanium(II) center.
Although some germylene and germanium gold(I) complexes have been reported, neither bis(germylenes) gold(I) complexes nor hetero ligands coordinated-gold(I) complexes containing germylene are known. Based on this literature survey, we made an attempt to extend the reactions of cyclic (alkyl)(amino) germylenes (CAAGe) \( \text{I} \) with transition metals such as gold(I), palladium(0), and palladium(II). In the cases where the reactions of CAAGe \( \text{I} \) with other transition metals were successful, the corresponding products were further investigated to gain an insight into their geometries and electronic structures, as well as the possibility of their application as catalysts in organic chemistry.

**Scheme 5.11** Synthesis of bis(α-iminopyridine) germanium(II) gold(I) complex XXII.
5.2 Results and Discussions

5.2.1 Reaction of CAAGe I with triphenylphosphine gold(I) chloride

The reaction of CAAGe 1 with one equivalent of tetrahydrothiophene gold(I) chloride \( ((\text{THT})\text{AuCl}) \) in \( \text{C}_6\text{D}_6 \) at room temperature led to the formation of the corresponding germanium dichloride 2, and unreacted CAAGe 1. When 2.2 equivalents of \( (\text{THT})\text{AuCl} \) were utilized under the same reaction conditions, germanium dichloride 2 was obtained quantitively (Scheme 5.12), the gold nanoparticles were also observed after the reaction on the surface of NMR tube.

\[
\begin{align*}
\text{1a, } R = \text{Dipp} & \quad \text{Dipp = 2,6-Diisopropylphenyl} \\
\text{1b, } R = \text{Ad} & \quad \text{THT = tetrahydrothiophene}
\end{align*}
\]

\[
\begin{align*}
\text{1a, } R = \text{Dipp} & \quad \text{Dipp = 2,6-Diisopropylphenyl} \\
\text{1b, } R = \text{Ad} & \quad \text{THT = tetrahydrothiophene}
\end{align*}
\]

\[
\begin{align*}
\text{2a, } R = \text{Dipp; } 100\% & \quad \text{2b, } R = \text{Ad; } 100\%
\end{align*}
\]

Scheme 5.12 Reactions of CAAGe 1 with (THT)AuCl.

In contrast, when CAAGe 1a and 1b were treated with triphenylphosphine gold(I) chloride, insertion into the Au–Cl bond led to the formation of 3a and 3b in 92% and 94% yield respectively (Scheme 5.13). Single crystals of 3a and 3b were grown by the volatilization method at room temperature in benzene, and their solid-state structure of 3a and 3b were determined by single crystal X-ray diffraction analysis (Figure 5.3). The Ge1–Au1 distances of 2.4037(4) Å in 3a and 2.4000(5) Å in 3b are similar to the known Au–Ge(IV) bond lengths, but significantly longer than Ge(II)–Au distances in VIII and X (2.3449(3) Å and 2.346(2) Å, respectively). previously reported Ge(II)–Au distances. The Ge–Au–P bond angle in 3a is 173.08(3) °, which indicates a nearly linear geometry. The Au atoms are not coplanar with the five-membered ring. The dihedral angle of the five-membered ring plane and Au1–Ge1 bond in 3a is 51.272 °, which is close to that in 3b (52.183 °).
Scheme 5.13 Reactions of CAAGe 1a and 1b with triphenylphosphine gold(I) chloride.

Figure 5.3 Solid state structures of 3a and 3b. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: 3a) Au1-P1 2.3174(8), Au1-Ge1 2.4037(4), Cl1-Ge1 2.2669(9), Ge1-N1 1.875(3), C15-Ge1 2.000(4), C13-N1 1.386(5), C13-C14 1.339(5), C14-C15 1.524(5), C1-N1 1.434(5); P1-Au1-Ge1 173.08(3), Cl1-Ge1-Au1 105.01(3), N1-Ge1-C15 90.25(14), 3b) Au1-P1 2.3066(12), Au1-Ge1 2.4000(5), Ge1-N1 1.866(4), Ge1-C1 1.991(4), Ge1-Cl1 2.2704(13), C1-C2 1.510(6), C1-Si1 1.897(5), C1-Si2 1.897(5), C2-C3 1.355(6), C3-N1 1.389(6), C4-N1 1.468(8); P1-Au1-Ge1 167.62(3), N1-Ge1-C1 90.97(18), Cl1-Ge1-Au1 123.59(14).

5.2.2 Reaction of germylene 1 with NHC gold(I) chloride

The reaction of CAAGe 1 with a stoichiometric amount of N-heterocyclic carbene gold(I) chloride was conducted at ambient temperature in benzene. Similar to the aforementioned reaction with Ph₃PAuCl, the insertion of 1 into the Au–Cl bond took place and the corresponding gold(I) complexes 4 were obtained in high yields (Scheme 5.14).
Colorless single crystals of 4a and 4b were obtained by volatilization with chloroform at room temperature. Their solid-state structures were determined by single crystal X-ray diffraction analysis and are shown in Figure 5.4. The Ge1–Au1–C1 bond angle of 4a is 173.08(3)° which is more acute than that of 4b (177.37(11)°). The differences in structural parameters of these complexes may likely be a result of the steric effect of the bulky adamantyl group. The Ge1–Au1 bond length of 4a (2.3892(5) Å) is slightly longer than that in 4b (2.3877(4) Å). However, the Ge1–Au1 bond length in 4a and 4b are shorter than that of 3 and the previously reported Ge(IV)–Au bond length.34-35, 40
**Figure 5.4** Solid state structures of 4a and 4b. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: 4a Au1-C1 2.058(4), Au1-Ge1 2.3892(5), C1-N3 1.348(6), C1-N2 1.354(6), C15-Ge1 2.012(4), Cl1-Ge1 2.2696(12), Ge1-N1 1.882(4); C1-Au1-Ge1 171.52(12), N3-C1-N2 105.4(3), Cl1-Ge1-Au1 101.16(3), N1-Ge1-C15 89.91(17); 4b Au1-C1 2.059(4), Au1-Ge1 2.3877(4), C1-N3 1.865(3); C1-Au1-Ge1 177.37(11), N1-Ge1-C15 89.88(16), Cl1-Au1-Ge1 104.77(3).

In the $^1$H NMR spectrum of 4a, two multiplet peaks for the CH of isopropyl groups of the NHC ligand appear at 2.71 ppm and 2.56 ppm, while one singlet was observed at 2.65 ppm for these protons in 4b; one singlet for the skeleton CH of NHC ligand appears at 7.22 ppm in 4b, while the corresponding protons are separated into two doublets peaks appearing at 7.08 ppm and 6.76 ppm in 4a (Figure 5.5).
Figure 5.5 $^1$H NMR spectra of 4a and 4b.

5.2.3 Reaction of germanium gold(I) complexes with silver reagents

With the successful synthesis of germanium gold(I) complexes 3 and 4, these complexes were then utilized for the synthesis of a cationic gold(I) complex supported by germylene and NHC. First, the reactions of 3a with AgX (X = BF$_4$, SbF$_6$, PF$_6$ and Al(OC(CF$_3$)$_3$)$_4$) were performed at ambient temperature in CDCl$_3$. After work-up, unidentifiable products were obtained. Meanwhile, the reactions of 4a with AgX (X = BF$_4$, SbF$_6$, PF$_6$ and Al(OC(CF$_3$)$_3$)$_4$) at room temperature in CDCl$_3$ afforded the corresponding gold(I) complexes 5 (Scheme 5.15). The complex 5d was characterized by NMR spectroscopy and single crystal X-ray diffraction analysis (Figure 5.6). Complex 4b was also reacted with AgX (X = BF$_4$, SbF$_6$, PF$_6$ and Al(OC(CF$_3$)$_3$)$_4$) under the same conditions, which unfortunately led to its decomposition.
Scheme 5.15 Reactions of germanium gold(I) complexes 4a with silver reagents.

5d possesses a nearly linear Ge1–Au1–C1 skeleton (176.62(15)°). The dihedral angle between the CAAGe five-membered ring and the NHC plane is 31.335°, which may be a result of the steric effect that resists the π conjugation of both planes. The Ge1–Au1 bond distances (2.3634(6) Å) were found to be slightly shorter than the Au–Ge bonds in XX (2.423(2) Å) and those in XXII (2.3857(6) Å) but longer than that in XX (2.346(2) Å). Complex 5d has remarkably shorter Ge1–N1 bond distances (1.807(5) Å) in comparison with that in 1a (1.859(11) Å), indicating an enhanced donation of the N lone pair electrons to the Ge atom.
**Figure 5.6** Solid-state structure of 5d. Hydrogen atoms and counter ion are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [º]: Au1-C22 2.047(6), Au1-Ge1 2.3634(6), C15-Ge1 1.925(6), Ge1-N1 1.807(5), C22-N2 1.337(7), C22-N3 1.346(7); C22-Au1-Ge1 176.62(15), N2-C22-N3 105.7(5), N1-Ge1-C15 91.2(2).

In order to investigate the electronic nature of 5d, density functional theory (DFT) calculations (at the B3LYP/6-31G(d,p) level for Ge, Si, C, N, H and M05-2X/LANL2DZ level for Au) on the cationic part of compound 5d were performed. According to NBO analysis, the Wiberg bond indices for the Ge–Au and C–Au bonds were 0.68 and 0.44, respectively. This suggested that the interaction between germylene and Au centre is stronger than that between Au and carbene. The HOMO–7 corresponds to the σ-donation of electron pairs from the Ge and C to gold(I), in which the latter is energetically stabilized by both carbene and germylene ligands (Figure 5.7a). The π-interaction between the Ge p_z orbitals and empty p-orbitals of carbene moiety can be observed clearly (LUMO, Figure 5.7b).
5.2.4 A brief introduction to the chemistry of germylene palladium complexes

The formation of germylene palladium(0) complex XXIVa was first synthesized by Hitchcock and co-workers in 1985 through the reaction of acyclic diamino germylene XXIII with [Pd(cod)Cl$_2$] under the mild condition in toluene, where the platinum analogues of XXIVb was also obtained by the reaction of [Pt(cod)Cl$_2$] and excess of XXIII (Scheme 5.16).$^{43}$

\[
\begin{align*}
\text{Me}_3\text{Si} &\text{N} \quad \text{Me}_3\text{Si} \text{N} \\
\text{Ge:} &+ \quad \text{M(cod)Cl}_2 \quad \text{toluene} \quad \text{r.t.} \\
\text{XXIII} &\quad \text{M} = \text{Pd, Pt} \\
\text{XXIVa: M} = \text{Pd; XXIVb: M} = \text{Pt}
\end{align*}
\]

Scheme 5.16 Formation of germylene metal complexes XXIV.

The reactions of acyclic diamino germylene XXIII with palladium(0) complexes have been reported by Holl and co-workers in 2002. The XVIII was reacted with 1 equivalent of tetrakis(phosphine) palladium(0) led to the formation of germylene palladium complex XXV (Scheme 5.17).$^{44}$
Scheme 5.17 Reactions of germylene XXIII with palladium(0) complexes.

The chemical behavior of dimeric germylene XXVI in relation to Pd(0) and Pd(II) complexes was studied by Zaitsev et al., where they carried out the reaction of XXVI with Pd(PPh₃)₄ resulting in tetrakis(germylene) palladium(0) complex XXVII and bis(phosphine)-mono(germylene) palladium(0) complex XXVIII (Scheme 5.18a). When XXVI was treated with Pd(PPh₃)₂Cl₂ at ambient temperatures in toluene, XXVII and Ge(IV) XXIX were obtained, as a result of the oxidation/reduction process (Scheme 5.18b).

Scheme 5.18 Reaction of dimeric germylene XXVI with Pd(0) and Pd(II) complexes.

5.2.5 Reaction of germylene 1a with palladium complexes

As CAAGe 1a has a high-lying HOMO−1 and low-lying LUMO, we conceived of a bis(germylene 1a) palladium(0) complex, which is different with the examples mentioned. The reaction of 1a with tetrakis(triphenylphosphine) palladium(0) was first carried out in benzene
(Scheme 5.19a) to obtain germylene bis(triphenylphosphine) palladium(0) 6. The structure of 6 was determined by NMR spectroscopy and single crystal X-ray diffraction analysis (Figure 5.8). When two equivalents of 1a were reacted with one equivalent of bis(triphenylphosphine) palladium(II)dichloride at ambient temperature in $\text{C}_6\text{D}_6$ for 1 h, palladium(0) complex 6 was obtained, albeit in a lower yield (31%) (Scheme 5.19b).

The Ge1–Pd1 bond distance of 6 (2.3539(7) Å) is strikingly longer than that in XXIV (2.330(5) Å) and slightly shorter than the Au1–Ge1 bond length in 5d (2.3634(6) Å). The Ge1–Pd1–P1 bond angle for 6 is 124.34(4)°, which is similar to that observed in the case of XXIV (125.66(2)°). The P1–Pd1–P2 bond angle is 119.80(5)°, which is also close to that in XXIV (119.45(4)°). The Ge1–N1 bond distance of 6 (1.870(4) Å) is slightly longer than that in 1a (1.859(11) Å) and significantly longer than that in 5d (1.807(5) Å), which indicated that the donation of electron density from the N atom to the empty $p$-orbital of Ge atom was subdued in complex 6 and enhanced in complex 5d.

Scheme 5.19 Reactions of CAAGe 1a with phosphine palladium complexes.
Figure 5.8 Solid state structure of 6. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ge1-Pd1 2.3539(7), P1-Pd1 2.3112(13), P2-Pd1 2.3332(13), Ge1-N1 1.870(4), C7-Ge1 1.995(5); N1-Ge1-C7 88.41(18), P1-Pd1-P2 119.80(5), P1-Pd1-Ge1 124.34(4), P2-Pd1-Ge1 115.82(4).
5.3 Conclusion

The reactions of CAAGe 1 with various gold(I), palladium(0) and palladium(II) complexes have been examined. The Au–Cl bond insertion products [ClGe–Au–PPh₃] 3 and [ClGe–Au–NHC] 4 were formed in the reactions of germynes 1 with triphenylphosphine gold(I) chloride and NHC gold(I) chloride respectively. The reactions of 4a with various silver reagents afforded the corresponding [Ge–Au–NHC]•X complex 5. Furthermore, the reaction of 1a with Pd(PPh₃)₄ resulted in the formation of germyle bis(triphenylphosphine) palladium(0) 6, which was also formed by the reaction of 1a with Pd(PPh₃)₂Cl₂.
5.4 Experimental Section

5.4.1 General Information

All reactions were performed under an atmosphere of argon by using standard Schlenk or dry box techniques; solvents were dried over sodium metal, potassium metal or CaH₂. All the substrates were obtained from the commercial sources or synthesized following literature procedures. ¹H, ¹³C, ¹⁹F and ³¹P spectra were obtained with AVIII 400MHz BBFO1 spectrometer at 298 K. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Coupling constants J are given in Hz. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with an OpticMelt Stanford Research System.

5.4.2 Reaction of germylene 1 with (THT)AuCl

(THT)AuCl (0.02 mmol, 6.5 mg) and 1 (0.01 mmol) were mixed in a sealed Young-NMR tube and the reaction mixture was shaken in C₆D₆ (0.5 mL) for 5 min at room temperature. Compounds 2 was then determined by NMR spectroscopy.

5.4.3 Reaction of germylene 1 with Ph₃PAuCl

Ph₃PAuCl (0.10 mmol, 50 mg) and 1 (0.10 mmol) were mixed in benzene (2 mL) and the reaction mixture was stirred for 1 h at room temperature. After that, the solvent was removed under vacuum, the mixture was washed with hexane to remove soluble part. The volatile was removed under vacuum, compound 3 was obtained as colorless solid: 3a (86 mg, 92%), 3b (85 mg, 94%).

3a: Mp: 157 °C (dec); ¹H NMR (400 MHz, C₆D₆) δ 7.24 (tt, J = 14.8, 7.4 Hz, 9H, Ar-H), 7.04 – 6.94 (m, 3H, Ar-H), 6.90 (m, 6H, Ar-H), 6.74 (d, J = 5.2 Hz, 1H, CH), 5.00 (d, J = 5.2
Hz, 1H, CH), 4.25 (dt, $J = 13.3, 6.5$ Hz, 1H, CH), 4.08 (dt, $J = 13.1, 6.5$ Hz, 1H, CH), 1.58 (d, $J = 6.6$ Hz, 3H, CH$_3$), 1.42 (d, $J = 6.6$ Hz, 3H, CH$_3$), 1.26 (d, $J = 6.5$ Hz, 3H, CH$_3$), 1.07 (d, $J = 6.9$ Hz, 3H, CH$_3$), 0.64 (s, 9H, Si(CH$_3$)$_3$), 0.49 (s, 9H, Si(CH$_3$)$_3$); $^{13}$C NMR (101 MHz, C$_6$D$_6$) $\delta$ 149.02 (C$^\beta$), 146.32 (C$^\alpha$), 142.48 (C$^\alpha$), 141.79 (CH), 134.06 (CH), 133.92 (CH), 131.11 (CH), 129.05 (CH), 128.94 (CH), 127.97 (CH), 125.83 (CH), 124.92 (CH), 122.58 (CH), 98.88 (CH), 37.22 (C$^\alpha$), 29.05 (CH$_3$), 28.02 (CH$_3$), 26.16 (CH$_3$), 24.97 (CH$_3$), 22.96 (CH$_3$), 2.51 (Si(CH$_3$)$_3$), 1.35 (Si(CH$_3$)$_3$); $^{31}$P NMR (162 MHz, C$_6$D$_6$) $\delta$ 46.29 (PPh$_3$); HRMS (ESI): m/z calcd for C$_{36}$H$_{52}$AuClGeNPSi$_2$: 927.1942, [(M+H)]$^+$; found: 928.1945.

3b: Mp: 149 °C (dec); $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 7.36 (m, 6H, Ar-H), 7.08 (d, $J = 5.5$ Hz, 1H, CH), 6.99 – 6.82 (m, 9H, Ar-H), 5.11 (d, $J = 5.4$ Hz, 1H, CH), 2.35 (q, $J = 11.1$ Hz, 6H, CH$_2$), 2.02 (s, 3H, CH), 1.69 – 1.50 (m, 6H, CH$_2$), 0.66 (s, 9H, Si(CH$_3$)$_3$), 0.47 (s, 9H, Si(CH$_3$)$_3$); $^{13}$C NMR (101 MHz, C$_6$D$_6$) $\delta$ 134.67 (CH), 134.09 (CH), 133.95 (CH), 131.18 (CH), 131.16 (CH), 130.31 (C$^\beta$), 129.83 (C$^\alpha$), 129.09 (CH), 128.98 (CH), 98.85 (CH), 54.05 (C$^\alpha$), 46.19 (CH$_2$), 36.68 (CH$_2$), 30.39 (CH), 2.62 (Si(CH$_3$)$_3$), 1.30 (Si(CH$_3$)$_3$); $^{31}$P NMR (162 MHz, C$_6$D$_6$) $\delta$ 46.16 (PPh$_3$); HRMS (ESI): m/z calcd for C$_{37}$H$_{50}$AuClGeNPSi$_2$: 901.1785, [(M+H)]$^+$; found: 902.1864.

5.4.4 Reaction of germylene 1 with NHAuCl

The mixture of NHAuCl (0.10 mmol, 62 mg) with 1 (0.10 mmol) was stirred in benzene (2 mL) at room temperature for 1 h. After the solvent was removed under vacuum, the mixture was washed with hexane to remove unreacted germylene 1. The volatile was then removed under vacuum, compound 4 was obtained as colorless solid: 4a (101 mg, 96%), 4b (95 mg, 93%).

4a: Mp: 187 °C (dec); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (t, $J = 7.8$ Hz, 2H, Ar-H), 7.30 (d, $J = 1.3$ Hz, 1H, Ar-H), 7.22 – 7.14 (m, 4H, Ar-H), 7.09 – 7.04 (m, 2H, Ar-H), 6.80 – 6.72 (m, 1H, CH), 6.27 (d, $J = 5.2$ Hz, 1H, CH), 4.60 (d, $J = 5.2$ Hz, 1H, CH), 3.61 (dt, $J = 13.6, 6.8$ Hz, 1H, CH), 3.22 (dt, $J = 13.8, 6.9$ Hz, 1H, CH), 2.71 (dt, $J = 13.7, 6.9$ Hz, 2H, CH), 2.56 (dt, $J =
13.7, 6.8 Hz, 2H, CH), 1.30 (d, J = 6.9 Hz, 6H, CH₃), 1.22 (d, J = 6.9 Hz, 6H, CH₃), 1.16 (d, J = 6.7 Hz, 3H, CH₃), 1.13 – 1.05 (m, 15H, CH₂), 0.83 (d, J = 6.8 Hz, 3H, CH₃), 0.43 (d, J = 7.0 Hz, 3H, CH₃), 0.12 (s, 9H, Si(CH₃)₃), -0.11 (s, 9H, Si(CH₃)₃); ¹³C NMR (101 MHz, CDCl₃) δ 197.21 (Ccarbene), 148.78 (C¹), 146.74 (C²), 145.35 (C³), 145.31 (C⁴), 142.46 (C⁵), 140.64 (C⁶), 134.17 (C⁷), 130.42 (CH), 124.64 (CH), 124.50 (CH), 124.23 (CH), 123.54 (CH), 123.27 (CH), 122.27 (CH), 98.54 (CH), 35.38 (C⁸), 28.81 (CH₃), 28.71 (CH₃), 27.91 (CH), 27.51 (CH), 26.27 (CH₃), 25.89 (CH), 24.50 (CH₃), 24.47 (CH₂), 24.30 (CH₃), 24.16 (CH), 23.74 (CH₃), 22.93 (CH), 2.53 (Si(CH₃)₃), 1.00 (Si(CH₃)₃); HRMS (ESI): m/z calcd for C₄₈H₂₅AuClGeN₃Si₂: 1053.3903. [(M+H)]⁺; found: 1054.3987.

4b: Mp: 182 °C (dec); ¹H NMR (400 MHz, CDCl₃) δ 7.50 (t, J = 7.8 Hz, 2H, Ar-H), 7.33 (d, J = 8.1 Hz, 4H, Ar-H), 7.22 (s, 2H, CH), 6.67 (d, J = 5.4 Hz, 1H, CH), 4.57 (d, J = 5.4 Hz, 1H, CH), 2.65 (dt, J = 13.8, 6.9 Hz, 4H, CH₂), 1.85 (s, 3H, CH), 1.67 (d, J = 2.2 Hz, 6H, CH₂), 1.49 (d, J = 12.9 Hz, 6H, CH₂), 1.40 (dd, J = 11.1, 6.9 Hz, 12H, CH₂), 1.24 (dd, J = 8.5, 7.0 Hz, 12H, CH₂), 0.04 (s, 9H, Si(CH₃)₃), −0.26 (s, 9H, Si(CH₃)₃); ¹³C NMR (101 MHz, CDCl₃) δ 197.39 (Ccarbene), 145.53 (C¹), 145.36 (C²), 134.17 (CH), 134.03 (C³), 130.59 (CH), 129.04 (CH), 128.20 (C⁴), 124.31 (CH), 124.12 (CH), 123.44 (CH), 119.97 (CH), 98.85 (CH), 53.52 (C⁵), 45.22 (CH₂), 36.60 (CH₂), 33.31 (C⁶), 29.94 (CH), 28.91 (CH), 28.87 (CH), 24.61 (CH₃), 24.53 (CH₃), 24.22 (CH₃), 24.05 (CH₃), 2.39 (Si(CH₃)₃), 0.89 (Si(CH₃)₃); HRMS (ESI): m/z calcd for C₄₈H₂₇AuClGeN₃Si₂: 1027.3747. [(M+H)]⁺; found: 1028.3844.

5.4.5 Reaction of 4a with AgX

The mixture of gold(I) complex 4a (0.05 mmol, 50 mg) with AgX (0.05 mmol) (AgBF₄, 10 mg; AgSbF₆, 17 mg; AgPF₆, 13 mg) was carried out in CDCl₃ (0.5 mL) at room temperature for 5 min. After the mixture was monitored by NMR spectroscopy to determine the yield (5a 84%; 5b 61%; 5c 58%).

The mixture of gold(I) complex 4a (0.10 mmol, 105 mg) with AgAl(OC(F₃)$_2$)$_4$, 107 mg)
was carried out in CHCl₃ (2 mL) at room temperature for 5 min. After AgCl was filtered off, all volatiles were removed under vacuum to afford 5d as a yellow solid (183 mg, 93%). Mp: 244 °C (dec). ¹H NMR (400 MHz, CDCl₃) δ 7.55 (t, J = 7.8 Hz, 2H, Ar-H), 7.34 (d, J = 7.8 Hz, 1H, Ar-H), 7.28 (d, J = 2.8 Hz, 5H, Ar-H), 7.19 (d, J = 4.8 Hz, 1H, CH), 7.13 (d, J = 7.8 Hz, 2H, CH), 6.25 (d, J = 4.8 Hz, 1H, CH), 2.54 (dt, J = 13.8, 6.9 Hz, 2H, CH), 2.45 – 2.28 (m, 4H, CH), 1.22 (d, J = 6.9 Hz, 12H, CH₃), 1.08 (d, J = 6.8 Hz, 6H, CH₃), 0.72 (d, J = 6.9 Hz, 6H, CH₃), 0.05 (s, 18H, Si(CH₃)₃); ¹³C NMR (101 MHz, CDCl₃) δ 188.12 (C carbene), 145.46 (Cq), 144.00 (Cq), 143.81 (CH), 138.72 (Cq), 132.70 (CH), 128.43 (CH), 124.55 (CH), 124.42 (CH), 123.59 (Cq), 122.72 (CH), 119.80 (CH), 119.11 (Cq), 75.74 (Cq), 28.79 (CH), 27.97 (CH), 25.24 (Cq), 25.00 (CH₃), 23.59 (CH₃), 23.44 (CH₃), 1.87 (Si(CH₃)₃); ²⁹F NMR (376 MHz, CDCl₃) δ -75.46 (CF₃); HRMS (ESI): m/z calcd for [C₄₁H₇₃AuGeN₃Si₂]+: 1018.4220. [M]+; found: 1018.4235.

5.4.6 Reaction of germylene 1a with Pd(PPh₃)₂Cl and Pd(PPh₃)₄

Pd(PPh₃)₂Cl₂ (0.1 mmol, 71 mg) and 1a (0.2 mmol, 87 mg) were mixed in benzene (1 mL), and the mixture was stirred for 1 hour at room temperature. After the solvent was removed under vacuum, the mixture was washed with hexane. Recrystallization with benzene afford 6 as red crystal (66 mg, 31%).

Pd(PPh₃)₄ (0.1 mmol, 116 mg) and 1a (0.1 mmol, 44 mg) were mixed in benzene (1 mL), and the mixture was stirred for 1 hour at ambient temperature, then recrystallized with benzene to afford 6 as red crystal (85 mg, 81%).

Mp: 167 °C (dec). ¹H NMR (400 MHz, C₆D₆) δ 7.39 (dd, J = 9.0, 7.1 Hz, 10H, Ar-H), 7.26 (dd, J = 8.5, 6.5 Hz, 1H, Ar-H), 7.19 (d, J = 7.0 Hz, 2H, Ar-H), 7.07 (d, J = 4.6 Hz, 1H, CH), 6.98 – 6.84 (m, 20H, Ar-H), 5.80 (d, J = 4.6 Hz, 1H, CH), 3.57 (dt, J = 13.6, 6.8 Hz, 2H, CH), 1.21 (d, J = 6.8 Hz, 6H, CH₃), 0.78 (d, J = 6.8 Hz, 6H, CH₃), 0.28 (s, 18H, Si(CH₃)₃); ¹³C NMR (101 MHz, C₆D₆) δ 145.36 (CH), 145.23 (Cq), 144.61 (Cq), 138.72 (CH), 138.59 (CH), 138.47
(CH), 133.96 (CH), 133.87 (CH), 133.79 (CH), 128.31 (CH), 126.04 (CH), 123.52 (CH), 111.82 (CH), 71.69 (C), 28.15 (CH), 24.77 (CH₃), 23.84 (CH₃), 1.53 (Si(CH₃)₃); HRMS (ESI): m/z calcd for C₅₇H₆₇PdGeNP₂Si₂: 1063.2534. [(M+H)]⁺; found: 1064.2646.
5.4.6 $^1H$, $^{13}C$, $^{19}F$ and $^{31}P$ NMR Spectra

Figure 5.9 $^1H$ NMR spectrum of 3a

Figure 5.10 $^{13}C$ NMR spectrum of 3a
Figure 5.11 DEPT-135 spectrum of 3a

Figure 5.12 $^{31}$P NMR spectrum of 3a
Figure 5.13 $^1$H NMR spectrum of 3b

Figure 5.14 $^{13}$C NMR spectrum of 3b
Figure 5.15 DEPT-135 spectrum of 3b

Figure 5.16 $^{31}$P NMR spectrum of 3b
Figure 5.17 $^1$H NMR spectrum of 4a

Figure 5.18 $^{13}$C NMR spectrum of 4a
Figure 5.19 DEPT-135 spectrum of 4a

Figure 5.20 $^1$H NMR spectrum of 4b
Figure 5.21 $^{13}$C NMR spectrum of $4b$

Figure 5.22 DEPT-135 spectrum of $4b$
Figure 5.23 $^1$H NMR spectrum of 5

Figure 5.24 $^{13}$C NMR spectrum of 5
Figure 5.25 DEPT-135 NMR spectrum of 5

Figure 5.26 $^{19}$F NMR spectrum of 5
Figure 5.27 $^1$H NMR spectrum of 6

Figure 5.28 $^{13}$C NMR spectrum of 6
Figure 5.29 $^{31}\text{P}$ NMR spectrum of 6
5.5 Reference


18. Weinberger, D. S.; Melaimi, M.; Moore, C. E.; Rheingold, A. L.; Frenking, G.;


Chapter 6 Hydroamination of terminal alkynes with ammonia catalysed by 2-pyridyene gold(I) catalyst to construct pyridine derivatives

6.1 Introduction

Carbenes are neutral divalent species and have both nucleophilic and electrophilic abilities. Carbenes have been utilized in the synthetic chemistry as supporting ligands and compared with the electron-rich phosphine ligands from the viewpoint of the donating ability.\textsuperscript{1-4} DFT calculations on N-heterocyclic carbene (NHC)-metal complexes showed that σ donation of NHCs contributes approximately 70% to the overall orbital interaction energy whereas π-interactions including both π donation and π back-donation contribute the remaining 15-30%.\textsuperscript{5-7}

As the first metal-carbene complex, methoxyphenylmethylenetungsten (0) pentacarbonyl I was reported by Fisher et al. in 1964 and its structure was identified by X-ray diffractometry and NMR spectroscopy (Figure 6.1).\textsuperscript{8} They employed the same method to access the chromium (0), iron (0), and manganese (0) carbene complexes where the adjacent methoxy and phenyl groups were replaced by different alkoxy and alkyl groups.\textsuperscript{9}

![Figure 6.1 Synthesis of the first metal-carbene complex I.](image)

Since then various carbene complexes have been reported, while it was difficult to isolate free carbenes due to their intrinsic instability. The first stable carbene III was reported by Bertrand and co-workers in 1988. By the flash thermolysis of (trimethylsilyl)
[bis(diisopropylamino)phosphino]-diazomethane II at 250 °C under vacuum, carbene III was synthesized and it was stabilized by the adjacent phosphorous and silicon substituents (Figure 6.2).\textsuperscript{10-13}

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{N}_2 \\
\text{Me}_3\text{Si} & \quad \text{C} \quad \text{P(}N\text{Pr}_2)\text{)}_2 \\
\text{II} & \quad \text{III} \\
250 \, ^\circ \text{C} & \quad & 250 \, ^\circ \text{C}
\end{align*}
\]

\textit{Figure 6.2} Synthesis of the first carbene III.

Three years later, Arduengo and co-workers reported the synthesis of carbene IVa by the deprotonation of the corresponding imidazolium salt with sodium hydride at ambient temperature in THF with a catalytic amount of dimethyl sulfoxide (DMSO). The solid-state structure of IVa was unambiguously characterized by X-ray crystallographic analysis (Figure 6.3).\textsuperscript{14,15}

\[
\begin{align*}
\text{H} & \quad \text{N} \\
\text{H} & \quad \text{N} \\
\text{Cl} & \quad \text{NaH} \\
\text{THF} & \quad \text{DMSO (cat.)} \\
\text{Ad} & \quad \text{Ad} \\
\text{Ad} & \quad \text{Ad} \\
\text{IVa} & \quad \text{IVa}
\end{align*}
\]

\textit{Figure 6.3} Synthesis of carbene IVa.

This seminal discovery led to the great development of experimental and theoretical investigations on the synthesis and analysis of NHCs. Following the pioneering work by Arduengo, various stable NHCs have been developed (Figure 6.4)\textsuperscript{14,16-18}, which was usually stabilized by employing the bulky substituents.\textsuperscript{11} Moreover, Bertrand et al. have successfully developed cyclic (alkyl)(amino) carbenes (CAACs) IX where one of the adjacent amino groups was replaced with a quaternary carbon compared with NHCs V (Figure 6.4). They also investigated the reactivities and electronic properties by experimental and theoretical studies,
and uncovered that CAACs IX exhibit both stronger σ-donating and π-accepting ability than NHCs.\textsuperscript{19-21}

![Diagram of CAACs and NHCs](image)

**Figure 6.4** Selected examples of NHCs.

Homogenous transition-metal catalysts have been successfully applied to a range of hydroaminations.\textsuperscript{22-26} Thus far, metal complexes such as ruthenium,\textsuperscript{27-30} iridium,\textsuperscript{31-33} nickel,\textsuperscript{34} rhodium,\textsuperscript{31, 33, 35-37} palladium,\textsuperscript{38-41} and platinum,\textsuperscript{42-43} copper,\textsuperscript{44} silver,\textsuperscript{45} gold,\textsuperscript{46-49} and zinc\textsuperscript{50, 51} have been widely utilized. Gold(I) complexes are also known to excel in the hydroamination of alkynes.\textsuperscript{52-54}

The hydroamination of unsaturated substrates with ammonia has attracted much attention as the 100\% atom-economic synthetic approach for the construction of nitrogen carbon bonds, in which the total molecular mass of the reactants is the same as the molecular mass of products without any byproducts. The hydroamination of olefins with ammonia in an anti-Markovnikov addition was regarded as one of the top ten challenges for catalysis.\textsuperscript{55} Direct functionalization of ammonia is still a great challenge in synthetic chemistry because of the following reasons:

First, Werner complex afforded by the coordination of either ammonia or amine substrates to transition metal is usually inert. Second, the activation of the enthalpically strong N–H bond (107 kcal/mol) of ammonia requires harsh conditions such as high temperature and high pressure. Third, ammonia disfavor proton exchanges either to or from it, due to the moderate basicity of ammonia.\textsuperscript{56}
In 2008, the gold-catalyzed hydroamination of alkynes with ammonia\(^{48}\) was reported by Bertrand and co-workers, where CAACs IX have been employed as the supporting ligands in the gold complexes (Figure 6.5). Similar catalysis with hydrazine has also been reported.\(^{49}\)

![Figure 6.5](image)

*Figure 6.5* Hydroamination of alkynes with ammonia or hydrazine catalyzed by CAACAu(I) complexes.

The reported transition-metal catalytic reactions with ammonia can be classified into three cases. The first one involves tandem processes in which ammonia reacts with aldehyde without the ruthenium catalyst (Figure 6.6).\(^{57}\)

![Figure 6.6](image)

*Figure 6.6* The formation of amines and imines catalyzed by ruthenium catalyst.
The second one involves the catalytic processes during which ammonia reacts with the copper center to form a metal ammonia complex. Oxidative-addition and reductive-elimination of copper complexes with substrates occur subsequently to afford the final products. The substrates were limited to electron-poor heteroaromatic halides, and electron-poor arenes in these reactions (Figure 6.7). The selectivity of primary amines was not under control, the secondary amines were generated accompanying.

![Figure 6.7](image)

Figure 6.7 The formation of primary amines catalyzed by copper complexes.

The third is the catalytic hydroamination of unsaturated substrates, which has been mentioned in this chapter earlier. In this reaction, CAACs play an important role. Werner-type complexes generated by the reaction of pre-catalysts with ammonia was inert and prevented the use of ammonia as a substrate in the catalytic reaction. However, the CAACs possessed of both strong σ donor and π acceptor properties that enable the gold complex to liberate ammonia molecule and to activate alkynes effectively.

In 2011, G. Kovács and co-workers reported the theoretical studies on hydroamination of alkynes with ammonia catalyzed by CAAC-Au(I). They revealed that the mechanism involves three steps: 1) coordination of the unsaturated substrates to the cationic gold center; 2) nucleophilic attack of ammonia on the C≡C bond; 3) the proton transfer from ammonia to the unsaturated carbon (C=C) atom, which is the key step in this reaction (Figure 6.8).
Figure 6.8 The proposed mechanism of hydroamination catalyzed by CAAC-Au(I).

From the above theoretical studies on hydroamination, we can hypothesize that if a stronger σ donating and π accepting ligand is employed to replace with the CAACs ligand of XI, the catalytic activity of L→Au(I) complex will be promoted. In 2009, M. S. Nechaev et al reported the theoretical study on thermodynamic stability and ligand properties of NHCs using the DFT calculation. The representative samples include imidazolin-2-ylidene(IV), imidazolidin-2-ylidene(V), CAAC (IX), pyrazolin-3-ylidene (VI), pyridin-2-ylidene (XIII), and pyridin-4-ylidene (XIV) (Figure 6.9).
According to their calculation results, the HOMOs increase in the order \( IV < V < IX < VI < XIII < XIV \) from \(-4.73\) eV to \(-3.31\) eV, which are higher than the strong \( \sigma \)-donor phosphine \( \text{P}^3\text{Bu}_3 \) (\(-4.92\) eV).\(^{65}\) Experimentally, the C–O stretching frequencies of L→nickel carbonyl and L→iridium carbonyl complex have been analyzed, which indicated that NHCs complexes have lower frequencies than their phosphine counterparts.\(^{65-68}\) This result indicates that carbenes are stronger \( \sigma \)-donors than phosphines. It is interesting that pyridine-based carbenes XIII and XIV have by far low LUMO, indicating that they could readily accept the \( d \)-electrons of metals and serve as good \( \pi \)-acceptor ligands. Pyridylidene XIII also possesses a higher HOMO energy compared with NHCs, and even CAACs. Hence, XIII could be considered as a better \( \sigma \)-donating and \( \pi \)-accepting ligand instead of CAACs, and will balance the polarity of M–NH\(_3\) bond to promote substrate exchange, which is necessary for a turnover in catalysis and the stability of the complex.\(^{64,69-70}\)

Free and isolable pyridylidenes are not available so far. In 2012, Itami \textit{et al.} synthesized a 2-pyridylidene→Au(I) complex XV by the deprotonation of the corresponding pyridinium salts followed by the addition of Me\(_2\)SAuCl (Figure 6.10).\(^{71}\) It should be noted that no 2-pyridylidene species were observed in this reaction. There are two possibilities why 2-pyridylidene cannot be
isolated. First, the adjacent substituents were not bulky enough to stabilize the free pyridylidenes. The second possibility is considered from the electronic effect, the 2,6-dimethylphenyl can be thought as donor for the $\sigma$-$\pi$ conjugation between the $\sigma$-bond of methyl group and $\pi$-aromatic moieties, which will cause the thermodynamic stability going down.\textsuperscript{72-73}

![Figure 6.10 Synthesis of 2-pyridylidene gold complex XV.](image)

Hence, we designed a novel 2-pyridylidene featuring two 3,5-di-tert-butylphenyl groups which are bulkier than 2,6-dimethylphenyl groups on the pyridylidene ring hindering the dimerization or polymerization. It will possess strong $\sigma$-donating and $\pi$-accepting abilities that can be utilized as a ligand to prepare 2-pyridilidene-gold complex 1 (Figure 6.11).\textsuperscript{64} 2-pyridilidene-gold complex 1 is expected to be able to catalyze the hydroamination of unsaturated substrates with ammonia and conduct the regioselectivity of reaction for the bulky substituents.\textsuperscript{22,74}

![Figure 6.11 The new 2-pyridilidene-gold complex 1.](image)
6.2 Results and Discussions

The synthetic route to 2-pyridyilene gold complex 1 is shown in Scheme 6.1. Pyridinium salt 4 bearing bulky substituents on 1,3,5-positions was chosen as the precursor of 1. The reaction of 3,5-dibromopyridine with 2 equivalents of boronic acid in the presence of Pd(PPh₃)₄ and Ba(OH)₂ afforded the product 2 in 90% yield. The next reaction of 2 with 1-chloro-2,4-dinitrobenzene was carried out in ethanol at 90 °C for 4 days providing a Zincke salt 3 in 70% isolated yield. The chloride anion exchange reaction of 3 took place in the presence of silver reagent (AgOTf), and then the 2,4-dinitrophenyl group was replaced by a mesityl (1,3,5-trimethylphenyl) group at 150 °C in situ. Finally, the product 4 was obtained as a brown solid in 90% isolated yield.

![Scheme 6.1 Synthesis of pyridinium salt 4. (R₁ = Mes, R₂ = 3,5-Bu₂C₆H₃)](image)

With the precursor pyridinium 4 in hand, the deprotonation of 4 was carried out with lithium hexamethyldisilazide (LiHMDS) in THF at room temperature (Scheme 6.2). While no free 2-pyridyldiene was observed in this deprotonation reactions at all. When THTAuCl was added to the mixture of reaction, the corresponding 2-pyridyldiene–gold(I) complex 1 was obtained in 27% isolated yield. The structure of 1 has been confirmed by X-ray diffractometry (Figure 6.12).
and its characteristic signal for the carbon of carbene was observed at 187.8 ppm in the $^{13}$C NMR spectroscopy. The pyridylidene six-membered ring of 1 is coplanar (the sum of internal pentagon angles = 720°). It should be noted that the Au–C bond length of 1 (1.989 Å) is shorter than that of XV (2.0113 Å) which indicates the stronger interaction between the 2-pyridylidene ligand and gold in 1.

**Scheme 6.2** Synthesis of 2-pyridylen gold complex 1. (R$_1$ = Mes, R$_2$ = 3,5-tert-Bu$_2$-C$_6$H$_3$)

**Figure 6.12** Solid state structure of 1. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Au1-C1 1.989(4), Au1-Cl1 2.2842(11), C1-N1 1.373(5), C3-C4 1.394(5), C1-C5 1.424(5), C2-N1 1.355(5), C2-C3 1.378(5), C4-C5 1.383(6); C1-Au1-Cl1 177.84(12), N1-C1-Au1 119.9(3), C5-C1-Au1 125.3(3), C4-C5-C1 120.0(4), C2-C3-C4 116.3(4), C2-N1-C1 125.1(3), C5-C4-C3 122.9(4), N1-C2-C3 120.9(4), N1-C1-C5 114.8(4).

As mentioned in chapter 6.1, due to the strong σ-donor property of CAACs promoted the
leaving of ammonia and π-acceptor property of CAACs increased the activity of alkynes of gold(I) π-complexes, CAACs gold complex could catalyze the hydroamination of ammonia or hydrazine with unsaturated substrates such as C≡C double bonds and C≡C triple bonds. It has been well discussed in chapter 6.1 that 2-pyridylidenes possess stronger σ-donor and π-acceptor properties than CAACs. Therefore, it is expected that 2-pyridylidene-gold complex 1 has a better catalytic activity than CAACs gold complex XI in hydroamination. With 2-pyridylidene–gold(I) complex 1 in hand, we have initially carried out the catalytic hydroamination of ethynylbenzene 5a with ammonia in the presence of 1 (5 mol%) in order to compare its catalytic activity with XI (Scheme 6.3).  

![Scheme 6.3 Hydroamination of ethynylbenzene with ammonia catalyzed by complex 1.](image)

The reaction was carried out for 12 h, instead of the expected product 1-phenylethan-1-imine 6a, an unexpected product was observed from the NMR spectra. In the 13C NMR spectrum, a characteristic peak was detected at 45.0 ppm, which was assigned to CH2 carbon. Initially, the compound from the anti-Markovnikov addition of ammonia to ethynylbenzene 5a was proposed according to the NMR spectra. Interestingly, the product 2-benzyl-4,6-diphenylpyridine 7a was confirmed by NMR spectroscopy (Scheme 6.4). Pyridine derivatives are important class heterocyclic compounds in natural products, pharmaceuticals, and efficient materials. Historically, the synthesis of pyridine relies on the condensation of the amine with carbonyl compounds.
Pyridine derivatives are the important class of heterocyclic compounds in natural products, pharmaceuticals, and efficient materials. Historically, the synthesis of pyridine relies on the condensation of amines with carbonyl compounds, which is similar to many condensation methods. Ammonia was commonly utilized in the synthesis of pyridine derivatives. Autoxidation was also a necessary step for the aromatization. (Scheme 6.5).

In 2005, Craig and Henry reported the synthesis of alkyl-, aryl- and ester substituted pyridines. They utilized the ozonolysis of 1,6-dienes to afford ketones which further reacted with ammonia to afford the final products (Scheme 6.6). It was established in aza-heterocycle for the construction of pyridine ring.

Transition metal catalyzed cyclization and coupling reactions offer a series of new routes
to functionalize pyridine derivatives. In 2002, Larock and *et al.* reported that Pd(II) complex has been utilized to synthesize pyridine derivatives (Scheme 6.7). This reaction included two steps: a) the coupling reaction of haloalkenes with terminal alkynes catalyzed by palladium; b) cyclization catalyzed by CuI.

![Scheme 6.7](image)

Scheme 6.7 Synthesis of pyridines catalyzed by transition metals.

In 2005, Suzuki *et al.* reported the synthesis of pyridine derivatives. The reaction involved a titanium intermediate which reacted with substituted alkynes, and quenched by E+ to provide 2,3,4,6-tetrasubstituted pyridines (Scheme 6.8).

![Scheme 6.8](image)

Scheme 6.8 Synthesis of 2,3,4,6-tetrasubstituted pyridines.

In our case, the possible mechanism for the formation of 7a is shown in scheme 6.9. The initial step is the formation of 1-phenylethane-1-imine 6 via Markovnikov addition of NH3 to alkyne. Then, imine 6 attacks another alkyne activated by the gold complex, which undergoes Anti-Markovnikov addition affording the 1-phenyl-N-styrylethan-1-imine intermediate 12. 13 is considered as the tautomer of 12, which reacts with the third alkyne to generate 15 without the activity of cationic Au species and then undergoes an aromatization to generate the final product 7a.
To verify the hypothesized mechanism, the reaction of phenylacetylene 5a with 1-phenylethan-1-imine 6a has been carried out (Scheme 6.10). As expected, when a large excess of phenylacetylene 5a was treated with ammonia, 2-benzyl-4,6-diphenylpyridine 7a was obtained as the major product in 51% yield after 5 h, indicating that the 1-phenylethan-1-imine 6a was involved in the reaction process. Although attempts have been made to monitor the other reaction intermediates 12 by varying the reaction temperature, time, and substrates ratio, 2-benzyl-4,6-diphenylpyridine 7a was the only detectable product in this reaction.

Scheme 6.9 The mechanism of hydroamination proposed.

Scheme 6.10 Reaction of phenylacetylene 5a with 1-phenylethan-1-imine 6a.
The reaction of $^{13}$C-labeling alkyne $5a^*$ with ammonia has been carried out under the same condition in the presence of gold catalyst 1 affording the corresponding $7a^*$ (Scheme 6.11), which supported the proposed reaction mechanism (Scheme 6.9) upon the corresponding $^{13}$C NMR spectrum.

![Scheme 6.11 Reaction of $^{13}$C-labeling phenylacetylene $5a^*$ with ammonia.](image-url)

When the reaction conditions were optimized. At the beginning, the amount of ammonia was determined at 0.4 equivalent (Table 6.1, Entries 3, and 5-8). there was no reaction when the temperature was below 100 °C, and until it was heated at 150 °C giving the highest yield (Table 6.1, Entries 1-3). The impact of catalyst loading has been tested, and almost showed no effect on the reaction (Table 6.1, Entries 3 and 4). The optimized conditions were determined at 150 °C, 1 mol% of catalyst loading, and 0.4 equivalent of ammonia (Table 6.1, Entry 3). The reaction of $5a$ with a large excess of ammonia exclusively afforded 1-phenylethan-1-imine $6a$ (Table 6.1, Entry 8), indicating that the initial step was a Markovnikov hydroamination of an alkyne with ammonia.
Table 6.1 Optimization of reaction conditions for the construction of pyridine 7a.\(^a\)

![Chemical structure of 5a, 7a, and 6a](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst [mol%]</th>
<th>t [h]</th>
<th>T [°C]</th>
<th>NH(_3) [eq.]</th>
<th>Yield (7a) [%](^b)</th>
<th>Yield (6a) [%](^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>12</td>
<td>r.t.</td>
<td>0.4</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>12</td>
<td>100</td>
<td>0.4</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>12</td>
<td>150</td>
<td>0.4</td>
<td>43</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>6</td>
<td>150</td>
<td>0.4</td>
<td>41</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>12</td>
<td>150</td>
<td>0.8</td>
<td>26</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>12</td>
<td>150</td>
<td>2</td>
<td>10</td>
<td>45</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>12</td>
<td>150</td>
<td>10</td>
<td>8</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>12</td>
<td>150</td>
<td>100</td>
<td>0</td>
<td>75</td>
</tr>
</tbody>
</table>

Notes: a. Reaction condition 5a (1 mmol), C\(_6\)D\(_6\) (0.7 mL). b. Yield was determined by \(^1\)H NMR spectroscopy using 1,4-di-t-butylbenzene as an internal standard.

With the optimized reaction condition in hand, the scope of the catalytic reaction was briefly examined with a variety of terminal alkynes 5 involving electron-donating (Table 6.2, entries 3, 9 and 10) as well as electron-withdrawing aromatic groups (Table 6.2, entries 2, and 4-8). The corresponding products (5a-1) were obtained in 20%–48% yields. The relatively low yield of 5h was probably due to the extremely strong electron-withdrawing CF\(_3\)-group (Table 6.2, entry 8), inducing the weak basicity of imine 6h and impeding its addition to second alkynes (Scheme 6.5). 2-Ethynylthiophene and 3-ethynylthiophene also exhibited tolerance to the reaction conditions (Table 6.2, entries 11 and 12). We have also obtained two single crystals of 7b and 7g supporting our speculation for the structure of 7 (Figure 6.13).
Figure 6.13 Solid state structure of 7b (left) and 7g (right). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [º]: 7b) N1-C1 1.3492(95), C1-C2 1.3867(116), C2-C3 1.3828(124), C3-C4 1.3771(98), C4-C5 1.4184(116), C5-N1 1.3344(113), C1-C6 1.5297(144), C6-C7 1.5083(117); C1-C6-C17 115.435(801); 7g) C1-N1 1.365(13), C1-C2 1.391(14), C2-C3 1.387(14), C3-C4 1.415(15), C4-C5 1.379(14), C5-N1 1.349(13), C5-C18 1.521(15), C18-C19 1.511(16); C19-C18-C5 111.4(9).
Table 6.2 The construction of pyridine derivatives catalyzed by 1 from alkynes and ammonia.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>7 Yield b,c</th>
<th>Entry</th>
<th>Substrate</th>
<th>7 Yield b,c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5a</td>
<td>7a 43% (40%)</td>
<td>7</td>
<td>5g</td>
<td>7g 41% (38%)</td>
</tr>
<tr>
<td>2</td>
<td>5b Br</td>
<td>7b 38% (34%)</td>
<td>8</td>
<td>5h F&lt;sub&gt;3&lt;/sub&gt;C</td>
<td>7h 23% (19%)</td>
</tr>
<tr>
<td>3</td>
<td>5c</td>
<td>7c 33% (30%)</td>
<td>9</td>
<td>5i MeO</td>
<td>7i 30% (28%)</td>
</tr>
<tr>
<td>4</td>
<td>5d Cl</td>
<td>7d 31% (27%)</td>
<td>10</td>
<td>5j</td>
<td>7j 41% (37%)</td>
</tr>
<tr>
<td>5</td>
<td>5e Cl</td>
<td>7e 31% (28%)</td>
<td>11</td>
<td>5k</td>
<td>7k 20% (17%)</td>
</tr>
<tr>
<td>6</td>
<td>5f F</td>
<td>7f 45% (43%)</td>
<td>12</td>
<td>5l</td>
<td>7l 48% (45%)</td>
</tr>
</tbody>
</table>

Notes: a. Reaction condition 5 (1 mmol), ammonia (0.25 mmol), LAuCl and KB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (1 mol%), and C<sub>6</sub>D<sub>6</sub> (0.7 mL). b. Yields were determined by <sup>1</sup>H NMR spectroscopy using 1,4-di-t-butyldibenzene as an internal standard. c. Isolated yields were given in parentheses.

Based on the results in table 6.2, we attempted to extend this strategy by employing two different terminal alkynes for the construction of rather complex pyridine derivatives 16 (Table 6.3). It was noteworthy to mention that the electron withdrawing alkynes were attacked in the anti-Markovnikov addition step and in absence of the initiative Markovnikov addition with ammonia and final aromatization steps. Why did the electron withdrawing alkynes only
attend the anti-Markovnikov addition step? The basicity of imine 6 was the key point for the formation of the 1-phenyl-N-styrylethan-1-imine intermediate 12. The nucleophilic attack of imine 6 to another alkyne was blocked, if imine 6 was featuring an electron-withdrawing substituent (Scheme 6.12). When imine 6 fearing electron donating group reacts with the second alkyne substituted by electron withdrawing group, the reaction will be promoted to give complex pyridine derivatives 16. 16d was characterized by X-ray crystallographic analysis, which aided us to speculate the structure of 16 (Figure 6.14). 16 has similar bonds lengths and angles of a skeleton to that of 7.

**Figure 6.14** Solid state structure of 16d. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: N1-C12 1.3662(34), C11-C12 1.3646(35), C10-C11 1.3728(27), C9-C10 1.3862(33), C8-C9 1.3919(32), C8-N1 1.3616(27), C12-C13 1.512(34), C13-C14 1.5080(39); C12-C13-C14 114.654(206).
Scheme 6.12 The mechanism of formation on 16 proposed.

\[ \text{Ar}^1 = \text{The electron donating alkynes} \]
\[ \text{Ar}^2 = \text{The electron withdrawing alkynes} \]
**Table 6.3** Au-catalyzed three-component coupling reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>16 Yield</th>
<th>7 Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>16a 15%</td>
<td>7c 18%</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>16b 10%</td>
<td>7m 12%</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>16c 11%</td>
<td>7m 12%</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>16d  8%</td>
<td>7m 12%</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>16e 14%</td>
<td>7m 11%</td>
</tr>
</tbody>
</table>

Notes: a. Reaction condition 5 (1 mmol), ammonia (0.25 mmol), LAuCl 1 and KB(C₆F₅)₄ (1 mol%), and C₆D₆ (0.7 mL). b. Isolated yields were given.

The reaction of alkyne 5a with 1-phenylethan-1-imine 6a in the presence of LAuCl 1 and KB(C₆F₅)₄ afforded 2-benzyl-4,6-diphenylpyridine 7a as the major product in 51% yield rather than the anti-Markovnikov addition product. It encouraged us to extend the substrates by replacing the methyl group with bulk groups to increase the stability of 12.

In 2011 Toste and co-workers reported that the reaction of phenylacetylene 5a with N,1-diphenylmethanimine PhN=CHPh in the presence of gold catalyst afforded propargylamine where alkynes were nucleophiles (Scheme 6.13a). Four years later, Zhao et al. reported nickel-catalyzed intermolecular coupling between internal alkynes and aromatic N–H ketimines.
Reported reactions of imines with alkynes.

To our best knowledge, the anti-Markovnikov addition of benzophenone imines 17 to terminal alkynes 5 has never been reported so far. We first examined the reaction of terminal alkynes 5a with benzophenone imine 17a catalyzed by 1 and KB(C₆F₅)₄ under the similar reaction conditions to that of ammonia (Scheme 5.14a). A mixture of (Z)-1,1-diphenyl-N-styrylmethanimine 18a and 1,1-diphenyl-N-(1-phenylvinyl) methanimine 19a were generated after 1 hour, and the yield of the anti-Markovnikov adduct 18a was nearly identical to that of Markovnikov adduct 19a. When the reaction time was extended to 6 h, 19a gradually decomposed to an unidentified mixture under the reaction conditions. Finally, the highest yield of 18a was obtained at 51% for 6 h. To further probe the formation of the anti-Markovnikov product, a ¹³C-labeling experiment with a ¹³C-labeled phenylacetylene 5a* was performed, which decisively afforded 18a*(Scheme 6.14b).
When the reaction was carried out (Table 6.4, entry 1), the anti-Markovnikov product 18a was observed prior to Markovnikov product 19a in the early stage of the reaction, and the highest yield (51%) of 18a was obtained, and Markovnikov product 19a completely decomposed after 6 h. When 1-bromo-4-ethynylbenezene 5b and 4-ethynyltoluene 5c were introduced, the similar results were presented (Table 6.4, entries 2 and 3). The scope of the hydroimidination with respect to imines has been investigated, which involving various imine substrates such as p-methylphenyl groups 17b, p-fluorophenyl groups 17c, as well as methyl benzimidate 17d. The corresponding 2-aza-1,3-dienes 18a-l were afforded from the hydroimidination of these imines 17a-d with alkynes 5a–c in moderate yields (Table 6.4, entries 1-12). It should be noted that the formation of 18 and 19 from terminal alkynes and imines has never been reported so far. The reaction of 2,2,4,4-tetramethylpentan-3-imine (\(\text{Bu}_2\text{C}=\text{NH}\)) with 5a has also been performed, which gave a complex mixture. The two single crystals of 18h and 18i have also been obtained to support our speculation for the structure of 18 (Figure 6.15) and the anti-Markovnikov addition step.
Figure 6.15 Solid state structure of 18b (left) and 18g (right). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [º]: 18h C2-C3 1.4657(51), C1-C2 1.3470(67), C1-N1 1.4003(45), N1-C9 1.1294(51); C9-N1-C1 120.412(294), N1-C1-C2 122.561(323), C1-C2-C3 127.792(421); 18i C15-C16 1.4457(32), C14-C15 1.3366(35), C1-N1 1.2933(29), N1-C14 1.3877(30); C14-N1-C1 121.115(205), N1-C14-C15 123.547(231), C14-C15-C16 123.972(255).
Table 6.4 Au-catalyzed hydroimination of terminal arylalkynes

![Chemical Reaction](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>5</th>
<th>17</th>
<th>Time (h)</th>
<th>Yield (%)&lt;sup&gt;b,c&lt;/sup&gt;</th>
<th>Ratio (18:19)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5a (R = H)</td>
<td>17</td>
<td>6</td>
<td>18a 51(47)</td>
<td>6.2 : 1</td>
</tr>
<tr>
<td>2</td>
<td>5b (R = Br)</td>
<td>17a</td>
<td>6</td>
<td>18b 54(50)</td>
<td>100 : 0</td>
</tr>
<tr>
<td>3</td>
<td>5c (R = Me)</td>
<td>17b</td>
<td>6</td>
<td>18c 43(39)</td>
<td>100 : 0</td>
</tr>
<tr>
<td>4</td>
<td>5a (R = H)</td>
<td>17a</td>
<td>6</td>
<td>18d 40(37)</td>
<td>100 : 0</td>
</tr>
<tr>
<td>5</td>
<td>5b (R = Br)</td>
<td>17a</td>
<td>6</td>
<td>18e 48(44)</td>
<td>100 : 0</td>
</tr>
<tr>
<td>6</td>
<td>5c (R = Me)</td>
<td>17b</td>
<td>6</td>
<td>18f 42(37)</td>
<td>100 : 0</td>
</tr>
<tr>
<td>7</td>
<td>5a (R = H)</td>
<td>17a</td>
<td>6</td>
<td>18g 50(47)</td>
<td>100 : 0</td>
</tr>
<tr>
<td>8</td>
<td>5b (R = Br)</td>
<td>17a</td>
<td>6</td>
<td>18h 48(42)</td>
<td>100 : 0</td>
</tr>
<tr>
<td>9</td>
<td>5c (R = Me)</td>
<td>17a</td>
<td>5</td>
<td>18i 36(32)</td>
<td>100 : 0</td>
</tr>
<tr>
<td>10</td>
<td>5a (R = H)</td>
<td>17a</td>
<td>4</td>
<td>18j 51(47)</td>
<td>4.3 : 1</td>
</tr>
<tr>
<td>11</td>
<td>5b (R = Br)</td>
<td>17a</td>
<td>3</td>
<td>18k 55(51)</td>
<td>6.1 : 1</td>
</tr>
<tr>
<td>12</td>
<td>5c (R = Me)</td>
<td>17b</td>
<td>3</td>
<td>18l 43(39)</td>
<td>6.1 : 1</td>
</tr>
</tbody>
</table>

Notes: a. Reaction condition 5 (1 mmol), ammonia (0.25 mmol), LAuCl and KB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (1 mol%), and C<sub>6</sub>D<sub>6</sub> (0.7 mL). b. Yields were determined by <sup>1</sup>H NMR spectroscopy using 1,4-di-t-butylbenzene as an internal standard. c. Isolated yields are given in parentheses.

The anti-Markovnikov products 18 were stable enough to be isolated by chromatography, which encouraged us to extend the substrates. We further tested the reaction of 17a with diphenylacetylene, which afforded N-(1,2-diphenylvinyl)-1,1-diphenylmethanimine in 78% yield (Scheme 6.15).<sup>83</sup>
Scheme 6.15 Reaction of imine 17a with diphenylacetylene catalyzed by gold catalyst 1.
6.3 Conclusion

A new gold complex 1 featuring a pyrid-2-yli dine ligand was synthesized and fully characterized. 1 has been employed in hydroamination of alkynes with ammonia, which provided an efficient synthetic method for the construction of pyridine derivatives 7. 1 has also been utilized in the hydroimination of alkynes with imines, which indicated an apparent anti-Markovnikov regioselectivity to form 2-aza-1,3-dienes 18. A plausible mechanism involving both Markovnikov and Anti-Markovnikov addition was proposed and certified by the experimental studies.
6.4 Experimental Section

All manipulations were performed under an atmosphere of dry argon or nitrogen using standard Schlenk techniques unless otherwise stated. Solvents were dried by standard methods and distilled under nitrogen. $^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded on Bruker BBFO1 400 or BBFO2 400 spectrometers at 298 K. Mass spectra were performed at the NTU Mass Spectrometry Laboratory. X-ray analyses were performed using Bruker X8-APEX X-ray diffraction instrument with Mo-radiation.

6.4.1 Synthesis of compound 3,5-bis(3,5-di-tert-butylphenyl)pyridine 2

3,5-dibromopyridine (10 mmol, 2.35 g), (3,5-di-tert-butylphenyl)boronic acid (25 mmol, 5.85 g), Pd(PPh$_3$)$_4$ (0.5 mmol, 0.58 g), Ba(OH)$_2$ (40 mmol, 6.88 g) were dissolved in THF and H$_2$O (10:1, 180 mL, degassed). The mixture was refluxed overnight. After cooling to room temperature, ethyl acetate was added and the organic layer was dried over MgSO$_4$. The product was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 10:1) to afford 2 as a yellow solid (4.1 g, 90%). M.P. 146 °C; $^1$H NMR δ (400 MHz, CDCl$_3$): 1.43 (s, 36H, CH$_3$); 7.45-7.46 (d, J = 4 Hz, 4H, Ar-H); 7.53 (s, 2H); 8.02-8.03 (t, J = 4 Hz, 1H, Py-H); 8.80-8.81 (d, J = 4 Hz, 2H, Py-H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 31.3 (CH$_3$), 35.2 (CH$_3$)$_3$-C), 122.0 (CH), 122.5 (CH), 133.8 (CH), 137.6 (C°), 137.9 (C°), 147.2 (CH), 151.8 (C°). HRMS [M+H]$^+$ m/z Calcd for C$_{33}$H$_{46}$N : 456.3630. Found: 456.3638.

6.4.2 Synthesis of compound 3

Compound 2 (10 mmol, 4.55 g) and 1-chloro-2,4-dinitrobenzene (15 mmol, 3.0 g) were dissolved in ethanol (50 mL) and the mixture was heated at 90 °C for 4 days. After removal of the solvent, the product was purified by silica gel column (petroleum ether: ethyl acetate = 10:1, 500 mL; ethanol, 300 mL) to afford Zincke salt as a red solid (4.6 g, 70%). M.P. 184 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 1.41 (s, 36H, CH$_3$); 7.17 (s, 2H, Ar-H); 7.48 (d, J = 4Hz, 4H, Ar-H);
7.66 (t, J = 12 Hz, 2H, Ar-H); 8.75 (d, J = 8 Hz, 2H, Py-H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 17.6 (CH\(_3\)), 21.2 (CH\(_3\)), 31.5 (C(CH\(_3\))\(_3\)), 35.3 (C(CH\(_3\))\(_3\)), 122.7 (CH), 125.5 (CH), 130.5 (CH), 132.3 (C\(^q\)), 139.3 (C\(^q\)), 141.2 (CH), 142.2 (C\(^q\)), 143.1 (CH), 144.2 (C\(^q\)), 153.0 (C\(^q\)). HRMS [M+H]\(^+\) m/z Calcd for C\(_{39}\)H\(_{49}\)O\(_4\)ClN\(_3\): 658.3412. Found: 658.3416.

6.4.3 Synthesis of compound 4

Zincke salt 3 (10 mmol, 6.57 g) was dissolved in CHCl\(_3\) (80 mL) and 2.56 g (10 mmol) of AgOTf was added. The mixture was stirred at room temperature for 30 min. After filtration, the solvent was removed under vacuum and 2,4,6-trimethylaniline (15 mL) was added. The mixture was heated at 150 °C for 3 h. After distillation to remove excess 2,4,6-trimethylaniline, the residue was purified by chromatography (PE:EA = 3:1, 300 mL; ethanol, 200 mL) to give 5.1 g (90%) of 4 as a brown solid; M.P. 198 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 1.41 (s, 36H, C\(_3\)H\(_3\)); 2.22 (s, 6H, CH\(_3\)); 2.43 (s, 3H, C\(_3\)H); 7.18 (s, 2H, Ar-H); 7.28 (s, 2H, Ar-H); 7.52 (d, J = 8 Hz, 4H, Ar-H); 7.67 (t, J = 4 Hz, 2H, Ar-H); 8.76 (d, J = 8 Hz, 2H, Ar-H); 8.78 (d, J = 12 Hz, 2H, Py-H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 17.7(CH\(_3\)), 21.2(CH\(_3\)), 31.3 (C(CH\(_3\))\(_3\)), 35.2 (C(CH\(_3\))\(_3\)), 122.2(CH), 125.3(CH), 130.5(CH), 132.4 (C\(^q\)), 139.5 (C\(^q\)), 141.3(CH), 142.2 (C\(^q\)), 142.9(CH), 144.2 (C\(^q\)), 153.1 (C\(^q\)). HRMS [M+H]\(^+\) m/z Calcd for C\(_{43}\)H\(_{57}\)F\(_3\)NO\(_3\): 724.4011. Found: 724.4009.

6.4.4 Synthesis of compound 1

A THF solution of LiHMDS (115 mmol, 1.0 M, 115 mL) was added to a THF solution (20.0 mL) of pyridinium triflate 4 (38.0 mmol, 25.0 g). The mixture was stirred at room temperature for 20 min. Chloro(tetrahydrothiophene) gold(I) (38.0 mmol, 11.5 g) was added to the mixture. The solution was filtered and concentrated under vacuum. The crude product was purified by silica gel column chromatography (MeOH: CHCl\(_3\) = 1:20) and 1 was obtained as a pale-yellow crystal by recrystallization with CHCl\(_3\)/toluene at room temperature (6.8 g, 27%), M.P. 231 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 1.41-1.45 (d, J = 16 Hz, 36H, CH\(_3\)); 2.15 (s, 6H, CH\(_3\)); 2.41 (s,
3H, CH3); 7.10 (s, 2H, Mes-H); 7.38-7.39 (d, J = 4 Hz, 2H, Ar-H); 7.28(s, 2H, Ar-H); 7.61 (s, 2H, Ar-H); 7.62(d, J = 4 Hz, 2H, Ar-H); 7.79(d, J = 12 Hz, 2H, Ar-H); 8.32(d, J =8 Hz, 1H, p-C6H4); 8.39 (d, J = 4 Hz, 1H, o-C6H4).

13C NMR (100 MHz, CDCl3): δ 18.04 (CH3), 21.29 (CH3), 31.47 (CH3), 31.57 (CH3), 35.14 (C(CH3)3), 35.19 (C(CH3)3), 121.21 (CH), 122.93 (CH), 123.88 (CH), 123.95 (CH), 129.86 (CH), 132.22 (C6), 134.01 (C6), 136.94 (C6), 136.97 (CH), 138.33 (CH), 139.77 (C6), 139.93 (C6), 145.84 (C6), 151.10 (C6), 152.29 (C6), 152.63 (C6), 187.52 (Ccarbene).


6.4.5 Au-catalyzed construction of pyridine derivatives 7

**General procedure**: Complex LAuCl 1 (8 mg, 5 mol%) and KB(C₆F₅)₄ (7 mg, 5 mol%) were introduced in a Wilmad CQPV thick-walled (1.4 mm) NMR tube. The C₆D₆ (0.7 mL), 1,4-di-t-butylbenzene (0.2 mmol, 38 mg), the desired alkyne 5 (1 mmol) were added in this reaction. NH₃ (0.4 mmol, 6.8 mg) was carefully condensed at −60 °C. The reaction mixture was heated at 150 °C and monitored periodically by 1H NMR. Upon completion, the products were purified on triethylamine deactivated silica gel with the appropriate mixture of n-hexane and ethyl acetate.

![-diagram](image)

7a: Yellow oil; 40% yield (isolated); 1H NMR (400 MHz, CDCl3): δ = 8.11 (d, J = 7.1 Hz, 2H, Ar-H), 7.79 (d, J = 1.3 Hz, 1H, Ar-H), 7.64 (dd, J = 8.1, 1.3 Hz, 2H, Ar-H), 7.55 – 7.40 (m, 9H, Ar-H), 7.36 (t, J = 7.5 Hz, 2H, Ar-H), 7.28 (d, J = 1.3 Hz, 1H, Ar-H), 4.34 (s, 2H, CH₂); 13C NMR (100 MHz, CDCl3): δ = 161.4 (C6), 157.5 (C6), 149.8 (C6), 139.7 (C6), 139.7 (C6), 138.9 (C6), 129.3 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 127.2 (CH), 127.1 (CH), 126.4 (CH), 119.6 (CH), 116.5 (CH), 45.0 (CH2); HRMS (ESI): m/z calcd for C₂₄H₂₀N: 322.1596 [(M+H)]⁺; Found: 322.1595.
7a*: Yellow oil; 38% yield (isolated); ^1^H NMR (400 MHz, CDCl₃): δ = 8.10-8.05 (m, 2H, Ar-H), 7.60 (d, J = 7.0 Hz, 2H, Ar-H), 7.49-7.39 (m, 9H, Ar-H), 7.32 (t, J = 7.6 Hz, 3H, Ar-H), 7.24 (d, J = 7.0 Hz, 1H, Ar-H), 4.30 (dd, J = 7.0, 3.6 Hz, 2H, CH₂); ^1^C NMR (100 MHz, CDCl₃): δ = 161.4 (dd, J = 58.5, 10.2 Hz, C*), 119.5 (d, J = 58.4 Hz, C*), 116.5 (d, J = 9.0 Hz, C*); HRMS (ESI): m/z calcd for C_{21}H_{13}BrN: 325.1696 [(M+H)]^+; Found: 325.1702.

7b: Yellow solid; MP: 134 °C; 34% yield (isolated); ^1^H NMR (400 MHz, CDCl₃): δ = 7.86 (d, J = 8.5 Hz, 2H, Ar-H), 7.60 (s, 1H, Ar-H), 7.53 (dd, J = 8.6, 2.5 Hz, 4H, Ar-H), 7.38 (dd, J = 10.4, 8.5 Hz, 4H, Ar-H), 7.18 (d, J = 3.3 Hz, 1H, Ar-H), 7.15 (s, 1H, Ar-H), 7.11 (s, 1H, Ar-H), 4.13 (s, 2H, CH₂); ^1^C NMR (100 MHz, CDCl₃): δ = 161.1 (C⁰), 156.6 (C⁰), 149.0 (C⁰), 138.4 (C⁰), 138.2 (C⁰), 137.4 (C⁰), 132.3 (CH), 131.9 (CH), 131.7 (CH), 130.9 (CH), 128.7 (CH), 123.6 (C⁰), 123.6 (C⁰), 120.4 (C⁰), 119.5 (CH), 116.0 (CH), 44.3 (CH₂); HRMS (ESI): m/z calcd for C_{21}H_{13}BrN: 555.8911 [(M+H)]^+; Found: 555.8897.

7c: Yellow oil; 30% yield (isolated); ^1^H NMR (400 MHz, CDCl₃): δ = 7.96 (d, J = 8.2 Hz, 2H, Ar-H), 7.70 (d, J = 1.4 Hz, 1H, Ar-H), 7.50 (d, J = 8.1 Hz, 2H, Ar-H), 7.30-7.24 (m, 6H, Ar-H), 7.18 (d, J = 1.4 Hz, 1H, Ar-H), 7.12 (d, J = 7.8 Hz, 2H, Ar-H), 4.23 (s, 2H, CH₂), 2.41 (s, 3H, CH₃), 2.40 (s, 3H, CH₃), 2.32 (s, 3H, CH₃); ^1^C NMR (100 MHz, CDCl₃): δ = 161.5 (C⁰), 157.4 (C⁰), 149.5 (C⁰), 138.8 (C⁰), 138.7 (C⁰), 137.1 (C⁰), 136.8 (C⁰), 136.1 (C⁰), 135.7 (C⁰), 129.7 (CH), 129.4 (CH), 129.2 (CH), 129.1 (CH), 127.0 (CH), 126.9 (CH), 119.0 (CH), 115.9 (CH), 44.6 (CH₂), 21.3 (CH₃), 21.2 (CH₃), 21.1 (CH₃); HRMS (ESI): m/z calcd for C_{27}H_{28}N: 364.2065 [(M+H)]^+; Found: 364.2071.

7d: Colorless solid; MP: 118 °C; 27% yield (isolated); ^1^H NMR (400 MHz, CDCl₃): δ = 8.00 (d, J = 8.6 Hz, 2H, Ar-H), 7.68 (d, J = 1.3 Hz, 1H, Ar-H), 7.54 (d, J = 8.5 Hz, 2H, Ar-H), 7.48-7.42 (m, 4H, Ar-H), 7.29 (s, 4H, Ar-H), 7.19 (d, J = 1.3 Hz, 1H, Ar-H), 4.23 (s, 2H, CH₂); ^1^C NMR (100 MHz, CDCl₃): δ = 161.1 (C⁰), 156.5 (C⁰), 148.9 (C⁰), 137.8 (C⁰), 137.7 (C⁰), 136.9 (C⁰), 135.3 (CH), 135.2 (CH), 132.3 (CH), 130.5 (CH), 129.3 (CH), 128.9 (C⁰), 128.7 (C⁰), 191
128.3 (C\(^\circ\)), 119.4 (CH), 116.0 (CH), 44.1 (CH\(_2\)); HRMS (ESI): m/z calcd for C\(_{24}H_{17}Cl_3N\): 427.0427 [(M+H)]\(^+\); Found: 427.0427.

7e: Yellow oil; 28% yield (isolated); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) = 7.66 (dd, \(J = 7.5, 1.9\) Hz, 1H, Ar-H), 7.60 (d, \(J = 1.4\) Hz, 1H, Ar-H), 7.49-7.46 (m, 2H, Ar-H), 7.42-7.31 (m, 7H, Ar-H), 7.22 (td, \(J = 7.3, 1.8\) Hz, 2H, Ar-H), 7.15 (d, \(J = 1.4\) Hz, 1H, Ar-H), 4.44 (s, 2H, CH\(_2\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) = 159.2 (C\(^\circ\)), 156.3 (C\(^\circ\)), 147.3 (C\(^\circ\)), 139.2 (C\(^\circ\)), 137.9 (C\(^\circ\)), 137.0 (C\(^\circ\)), 134.3 (CH), 132.3 (CH), 131.8 (CH), 131.5 (CH), 131.0 (CH), 130.2 (CH), 130.1 (CH), 129.6 (CH), 129.5 (CH), 128.0 (CH), 127.1 (C\(^\circ\)), 127.0 (C\(^\circ\)), 126.9 (C\(^\circ\)), 123.2 (CH), 122.2 (CH), 42.0 (CH\(_2\)); HRMS (ESI): m/z calcd for C\(_{24}H_{17}Cl_3N\): 427.0427 [(M+H)]\(^+\); Found: 427.0427.

7f: Yellow oil; 43% yield (isolated); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) = 8.05 (dd, \(J = 8.9, 5.4\) Hz, 2H, Ar-H), 7.66 (d, \(J = 1.4\) Hz, 1H, Ar-H), 7.59 (dd, \(J = 8.8, 5.3\) Hz, 2H, Ar-H), 7.33 (dd, \(J = 8.6, 5.5\) Hz, 2H, Ar-H), 7.17 (m, 5H, Ar-H), 7.02 (t, \(J = 8.7\) Hz, 1H, Ar-H), 4.24 (s, 2H, CH\(_2\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) = 163.8 (d, \(J_{CF} = 195.5\) Hz, C\(^\circ\)), 163.5 (d, \(J_{CF} = 229.6\) Hz, C\(^\circ\)), 161.3 (d, \(J_{CF} = 172.2\) Hz, C\(^\circ\)), 161.3 (C\(^\circ\)), 156.6 (C\(^\circ\)), 149.0 (C\(^\circ\)), 135.6 (d, \(J_{CF} = 3.1\) Hz, C\(^\circ\)), 135.2 (d, \(J_{CF} = 3.1\) Hz, C\(^\circ\)), 134.7 (d, \(J_{CF} = 3.3\) Hz, C\(^\circ\)), 130.6 (d, \(J_{CF} = 7.9\) Hz, CH), 128.9 (d, \(J_{CF} = 5.5\) Hz, CH), 128.8 (d, \(J_{CF} = 5.4\) Hz, CH), 119.2 (CH), 116.0 (d, \(J = 21.5\) Hz, CH), 115.6 (d, \(J = 21.6\) Hz, CH), 115.3 (d, \(J = 21.2\) Hz, CH), 44.0 (CH\(_2\)); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) = −112.6 (m, 1F), −112.9 (m, 1F), −116.80 (m, 1F); HRMS (ESI): m/z calcd for C\(_{24}H_{17}F_3N\): 376.1313 [(M+H)]\(^+\); Found: 376.1308.

7g: Yellow solid; MP: 90 ºC; 38% yield (isolated); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) = 8.03 (td, \(J = 7.8, 1.7\) Hz, 1H, Ar-H), 7.82 (s, 1H, Ar-H), 7.45 (td, \(J = 7.7, 1.5\) Hz, 1H, Ar-H), 7.36 (dd, \(J = 13.4, 6.4\) Hz, 3H, Ar-H), 7.28 (s, 1H, Ar-H), 7.25-7.22 (m, 1H, Ar-H), 7.21 (s, 1H, Ar-H), 7.15 (d, \(J = 1.4\) Hz, 1H, Ar-H), 7.09 (s, 1H, Ar-H), 4.33 (s, 2H, CH\(_2\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) = 161.0 (d, \(J = 245.6\) Hz, C\(^\circ\)), 160.6 (d, \(J = 249.7\) Hz, C\(^\circ\)), 159.8 (d, \(J = 250.1\) Hz, C\(^\circ\)), 159.9 (C\(^\circ\)), 153.1 (C\(^\circ\)), 144.5 (C\(^\circ\)), 131.5 (d, \(J = 4.4\) Hz, CH), 131.3 (d, \(J = 2.9\) Hz, CH), 130.4
(m), 130.3 (CH), 128.3 (d, J = 8.0 Hz, CH), 127.5 (d, J = 11.6 Hz, C\text{\textsuperscript{\textalpha}}), 126.6 (d, J = 12.9 Hz, C\text{\textsuperscript{\textalpha}}), 126.4 (d, J = 16.0 Hz, C\text{\textsuperscript{\textalpha}}), 124.6 (d, J = 3.7 Hz, CH), 124.5 (d, J = 3.5 Hz, CH), 124.2 (d, J = 3.5 Hz, CH), 122.3 (d, J = 3.2 Hz, CH), 122.2 (d, J = 3.2 Hz, CH), 121.5 (d, J = 2.5 Hz, CH), 116.4 (d, J = 20.6 Hz, CH), 116.1 (d, J = 21.2 Hz, CH), 115.3 (d, J = 22.0 Hz, CH), 37.6 (d, J = 2.8 Hz, CH\text{\textalpha}); \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): \delta = −116.9 (m, 2F), −117.5 (m, 1F); HRMS (ESI): m/z calcd for C\textsubscript{23}H\textsubscript{17}F\textsubscript{3}N: 376.1313 [(M+H)]\textsuperscript{+}; Found: 376.1307.

\textbf{7h:} Yellow oil; 19\% yield (isolated); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta = 8.18 (d, J = 8.1 Hz, 2H, Ar-H\text{\textalpha}), 7.76 (d, J = 7.8 Hz, 3H, Ar-H\text{\textalpha}), 7.70 (d, J = 8.1 Hz, 2H, Ar-H\text{\textalpha}), 7.65 (d, J = 8.0 Hz, 1H, Ar-H\text{\textalpha}), 7.47 (d, J = 8.1 Hz, 2H, Ar-H\text{\textalpha}), 7.36 (d, J = 8.0 Hz, 2H, Ar-H\text{\textalpha}), 7.20 (d, J = 8.1 Hz, 2H, Ar-H\text{\textalpha}), 4.24 (s, 2H, CH\text{\textsubscript{2}}); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta = 156.7 (C\text{\textsuperscript{\textalpha}}), 154.8 (C\text{\textsuperscript{\textalpha}}), 143.4 (q, C\text{\textalpha}), 142.8 (q, C\text{\textalpha}), 142.0 (q, C\text{\textalpha}), 138.70 (CH), 130.4 (q, J = 38.2 Hz, C\text{\textalpha}), 129.55 (CH), 129.17 (CH), 127.18 (CH), 125.76 (q, J = 3.7 Hz, CH), 125.51 (q, J = 3.7 Hz, CH), 125.18 (q, J = 3.7 Hz, CH), 122.6 (q, C\text{\textalpha}), 118.5 (CH), 41.6 (CH\text{\textsubscript{2}}); \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): \delta = −63.3 (s, 1F), −63.5 (s, 1F), −63.5 (s, 1F); HRMS (ESI): m/z calcd for C\textsubscript{27}H\textsubscript{17}F\textsubscript{3}N: 526.1217 [(M+H)]\textsuperscript{+}; Found: 526.1212.

\textbf{7i:} Yellow oil; 28\% yield (isolated); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta = 7.68 (d, J = 1.3 Hz, 1H, Ar-H\text{\textalpha}), 7.25-7.22 (m, 3H, Ar-H\text{\textalpha}), 6.72 (d, J = 2.2 Hz, 2H, Ar-H\text{\textalpha}), 6.56 – 6.52 (m, 4H, Ar-H\text{\textalpha}), 6.34 (t, J = 2.3 Hz, 1H, Ar-H\text{\textalpha}), 4.21 (s, 2H, CH\text{\textsubscript{2}}), 3.87 (s, 6H, OCH\textsubscript{3}), 3.83 (s, 6H, OCH\textsubscript{3}), 3.76 (s, 6H, OCH\textsubscript{3}); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta = 161.2 (C\text{\textsuperscript{\textalpha}}), 161.1 (C\text{\textsuperscript{\textalpha}}), 160.9 (C\text{\textsuperscript{\textalpha}}), 160.8 (C\text{\textsuperscript{\textalpha}}), 157.1 (C\text{\textalpha}), 149.9 (C\text{\textalpha}), 141.8 (C\text{\textalpha}), 141.8 (C\text{\textalpha}), 141.0 (C\text{\textalpha}), 119.9 (CH), 116.7 (CH), 107.4 (CH), 105.5 (CH), 105.3 (CH), 100.1 (CH), 100.5 (CH), 98.2 (CH), 55.5 (CH\text{\textalpha}), 55.5 (CH\text{\textalpha}), 55.2 (CH\text{\textalpha}), 45.0 (CH\text{\textalpha}); HRMS (ESI): m/z calcd for C\textsubscript{36}H\textsubscript{32}NO\textsubscript{6}: 502.2230 [(M+H)]\textsuperscript{+}; Found: 502.2229.

\textbf{7j:} Yellow oil; 37\% yield (isolated); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta = 7.89 (s, 1H, Ar-H\text{\textalpha}), 7.85 (d, J = 7.8 Hz, 1H, Ar-H\text{\textalpha}), 7.72 (s, 1H, Ar-H\text{\textalpha}), 7.45 – 7.32 (m, 5H, Ar-H\text{\textalpha}), 7.22 (t, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 7.17 (t, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 7.04 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 6.88 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 6.65 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 6.22 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 5.89 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 5.56 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 5.22 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 4.95 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 4.62 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 4.29 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 4.06 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 3.83 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 3.60 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 3.37 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 3.14 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 2.91 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 2.68 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 2.45 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 2.22 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 1.99 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 1.76 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 1.53 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 1.30 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 0.87 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}), 0.64 (d, J = 8.3 Hz, 2H, Ar-H\text{\textalpha}).
Hz, 5H, Ar-H), 7.04 (d, J = 7.1 Hz, 1H, Ar-H), 4.26 (s, 2H, CH₂), 2.46 (s, 3H, CH₃), 2.42 (s, 3H, CH₃), 2.34 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 161.3 (C₅), 157.6 (C₅), 149.8 (C₅), 139.8 (C₅), 139.6 (C₅), 138.9 (C₅), 138.6 (C₅), 138.3 (C₅), 138.0 (C₅), 130.0 (CH), 129.5 (CH), 129.5 (CH), 128.8 (CH), 128.60 (CH), 128.4 (CH), 127.9 (CH), 127.8 (CH), 127.0 (CH), 126.2 (CH), 124.3 (CH), 124.2 (CH), 119.5 (CH), 116.6 (CH), 44.9 (CH₂), 21.61 (CH₃), 21.50 (CH₃), 21.44 (CH₃); HRMS (ESI): m/z calcd for C₁₇H₂₇N₂: 364.2065 [(M+H)]⁺; Found: 364.2062.

7k: Yellow oil; 17% yield (isolated); ¹H NMR (400 MHz, CDCl₃): δ = 7.68 (d, J = 3.2 Hz, 2H, Ar-H), 7.49-7.42 (m, 1H, Ar-H), 7.40 (t, J = 4.1 Hz, 2H, Ar-H), 7.23 (d, J = 1.2 Hz, 1H, Ar-H), 7.20 (dd, J = 4.9, 1.4 Hz, 1H, Ar-H), 7.1-7.11 (m, 2H, Ar-H), 6.97-6.95 (m, 2H, Ar-H), 4.38 (s, 2H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 160.5 (C₅), 152.9 (C₅), 145.0 (C₅), 142.9 (C₅), 141.5 (C₅), 141.5 (C₅), 128.4 (CH), 128.1 (CH), 127.8 (CH), 127.1 (CH), 126.9 (CH), 125.9 (CH), 125.5 (CH), 124.9 (CH), 124.6 (CH), 117.3 (CH), 113.2 (CH), 38.7 (CH₂); HRMS (ESI): m/z calcd for C₁₅H₁₄NS: 340.0288 [(M+H)]⁺; Found: 340.0290.

7l: Yellow oil; 45% yield (isolated); ¹H NMR (400 MHz, CDCl₃): δ = 7.95 (dd, J = 3.0, 1.2 Hz, 1H, Ar-H), 7.70 (dd, J = 5.0, 1.2 Hz, 1H, Ar-H), 7.62 (d, J = 1.4 Hz, 1H, Ar-H), 7.61 (dd, J = 2.5, 1.8 Hz, 1H, Ar-H), 7.43-7.35 (m, 3H, Ar-H), 7.27 (dd, J = 4.9, 3.0 Hz, 1H, Ar-H), 7.18 (d, J = 1.4 Hz, 1H, Ar-H), 7.10 (dd, J = 2.0, 1.0 Hz, 1H, Ar-H), 7.08 (dd, J = 4.9, 1.2 Hz, 1H, Ar-H), 4.23 (s, 2H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 160.9 (C₅), 153.7 (C₅), 144.0 (C₅), 142.47 (C₅), 140.0 (C₅), 139.6 (C₅), 128.7 (CH), 126.9 (CH), 126.4 (CH), 126.2 (CH), 125.9 (CH), 125.6 (CH), 123.7 (CH), 122.9 (CH), 121.8 (CH), 118.3 (CH), 115.3 (CH), 39.4 (CH₂); HRMS (ESI): m/z calcd for C₁₅H₁₄NS: 340.0288 [(M+H)]⁺; Found: 340.0290.

7m: Yellow oil; 14% yield (isolated); ¹H NMR (400 MHz, CDCl₃): δ = 8.02 (d, J = 8.5 Hz, 2H, Ar-H), 7.64 (d, J = 1.1 Hz, 1H, Ar-H), 7.56 (d, J = 8.8 Hz, 2H, Ar-H), 7.30 (d, J = 8.5 Hz, 2H, Ar-H), 7.13 (d, J = 1.0 Hz, 1H, Ar-H), 6.99 (dd, J = 12.1, 8.8 Hz, 4H, Ar-H), 6.86 (d, J = 8.6 Hz, 2H, Ar-H), 4.20 (s, 2H, CH₂), 3.87 (s, 3H, OCH₃), 3.85 (s, 3H, OCH₃), 3.79 (s, 3H, OCH₃);
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 161.5$ (C$^\circ$), 160.3 (C$^\circ$), 160.3 (C$^\circ$), 158.1 (C$^\circ$), 157.0 (C$^\circ$), 149.1 (C$^\circ$), 132.5 (C$^\circ$), 131.9 (C$^\circ$), 131.3 (C$^\circ$), 130.2 (CH), 128.3 (CH), 128.2 (CH), 118.2 (CH), 115.1 (CH), 114.3 (CH), 114.0 (CH), 113.9 (CH), 55.4 (OCH$_3$), 55.2 (OCH$_3$), 44.1 (CH$_2$); HRMS (ESI): m/z calcd for C$_{27}$H$_{28}$NO$_3$: 412.1913 [(M+H)]$^+$. Found: 412.1915.

16a: Colorless solid; Mp: 110 °C; 12% yield (isolated); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.95$ (d, $J = 8.1$ Hz, 2H, Ar-$H$), 7.74 (s, 1H, Ar-$H$), 7.57 (d, $J = 8.3$ Hz, 2H, Ar-$H$), 7.51 (m, 4H, Ar-$H$), 7.28 (m, 4H, Ar-$H$), 7.20 (s, 1H, Ar-$H$), 4.31 (s, 2H, CH$_2$), 2.42 (s, 3H, CH$_3$), 2.41 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 160.2$ (C$^\circ$), 157.9 (C$^\circ$), 150.0 (C$^\circ$), 144.08 (C$^\circ$), 139.2 (C$^\circ$), 139.1 (C$^\circ$), 136.9 (C$^\circ$), 135.9 (C$^\circ$), 129.9 (CH), 129.6 (CH), 129.6 (CH), 128.6 (q, $J = 31.8$ Hz, C$^\circ$), 127.1 (CH), 127.0 (CH), 125.8 (q, C$^\circ$), 125.5 (q, $J = 3.7$ Hz, CH), 119.2 (CH), 116.3 (CH), 44.8 (CH$_2$), 21.4 (CH$_3$), 21.3 (CH$_3$); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -62.3$ (s, 1F); HRMS (ESI): m/z calcd for C$_{27}$H$_{23}$NF$_3$: 418.1783 [(M+H)]$^+$. Found: 418.1779.

16b: Yellow oil; 10% yield (isolated); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.01$ (d, $J = 8.8$ Hz, 2H, Ar-$H$), 7.66 (s, 1H, Ar-$H$), 7.57 (d, $J = 8.7$ Hz, 2H, Ar-$H$), 7.43 (d, $J = 8.4$ Hz, 2H, Ar-$H$), 7.25 (d, $J = 5.3$ Hz, 2H, Ar-$H$), 7.13 (s, 1H, Ar-$H$), 7.00 (dd, $J = 8.8$, 6.8 Hz, 4H, Ar-$H$), 4.19 (s, 2H, CH$_2$), 3.88 (s, 3H, OCH$_3$), 3.86 (s, 3H, OCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 160.6$ (C$^\circ$), 160.5 (C$^\circ$), 157.4 (C$^\circ$), 149.4 (C$^\circ$), 139.0 (C$^\circ$), 132.5 (C$^\circ$), 131.7 (CH), 131.2 (C$^\circ$), 131.1 (CH), 128.5 (CH), 128.3 (CH), 120.3 (C$^\circ$), 118.4 (CH), 115.4 (CH), 114.6 (CH), 114.2 (CH), 55.5 (OCH$_3$), 55.5 (OCH$_3$), 44.4 (CH$_2$); HRMS (ESI): m/z calcd for C$_{28}$H$_{21}$NO$_3$Br: 460.0912 [(M+H)]$^+$; Found: 460.0911.

16c: Colorless oil; 10% yield (isolated); $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.01$ (d, $J = 8.9$ Hz, 2H, Ar-$H$), 7.66 (d, $J = 1.4$ Hz, 1H, Ar-$H$), 7.57 (d, $J = 8.8$ Hz, 2H, Ar-$H$), 7.34 (dd, $J = 8.7$, 5.5 Hz, 2H, Ar-$H$), 7.13 (d, $J = 1.4$ Hz, 1H, Ar-$H$), 7.00 (dd, $J = 9.3$, 7.9 Hz, 6H, Ar-$H$), 4.22 (s, 2H, CH$_2$), 3.88 (s, 3H, OCH$_3$), 3.86 (s, 3H, OCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 162.9$ (d, $J = 192.1$ Hz, C$^\circ$), 161.0 (C$^\circ$), 160.5 (d, $J = 3.1$ Hz, C$^\circ$), 157.3 (C$^\circ$), 149.4 (C$^\circ$), 135.7 (C$^\circ$), 135.6
(C⁹), 132.5 (C⁹), 131.3 (C⁹), 130.8 (d, J = 7.8 Hz, CH), 128.5 (d, J = 13.2 Hz, CH), 118.4 (CH), 115.5 (CH), 115.3 (CH), 115.3 (CH), 114.5 (CH), 114.2 (CH), 55.5 (OCH₃), 55.5 (OCH₃), 44.2 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃): δ = −117.1 (m, 1F); HRMS (ESI): m/z calcd for C₂₆H₂₃NFO₂: 400.1713 [(M+H)]⁺; Found: 400.1709.

**16d**: Colorless solid; Mp: 113 °C; 6% yield (isolated); ¹H NMR (400 MHz, CDCl₃): δ = 8.03 (d, J = 8.8 Hz, 2H, Ar-H), 7.69 (s, 1H, Ar-H), 7.58 (d, J = 8.8 Hz, 4H, Ar-H), 7.51 (d, J = 8.1 Hz, 2H, Ar-H), 7.17 (s, 1H, Ar-H), 7.01 (t, J = 8.2 Hz, 4H, Ar-H), 4.30 (s, 2H, CH₂), 3.88 (s, 3H, OCH₃), 3.86 (s, 3H, OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 160.6 (C⁹), 160.5 (C⁹), 160.0 (C⁹), 157.4 (C⁹), 149.5 (C⁹), 144.1 (C⁹), 144.1 (C⁹), 132.4 (C⁹), 131.1 (C⁹), 129.6 (CH), 128.5 (q, J = 32.1 Hz, C⁹), 128.4 (CH), 128.3 (CH), 127.8 (q, J = 261.9 Hz, C⁹), 125.5 (q, J = 3.7 Hz, CH), 118.5 (CH), 115.5 (CH), 114.6 (CH), 114.2 (CH), 55.5 (OCH₃), 55.5 (OCH₃), 44.8 (CH₂); ¹⁹F NMR (377 MHz, CDCl₃): δ = −62.3 (s, 1F); HRMS (ESI): m/z calcd for C₂₇H₂₃NO₂F₃: 450.1681 [(M+H)]⁺; Found: 450.1681.

**16e**: Colorless solid; Mp: 103 °C; 14% yield (isolated); ¹H NMR (400 MHz, CDCl₃): δ = 8.02 (d, J = 8.8 Hz, 2H, Ar-H), 7.67 (s, 1H, Ar-H), 7.58 (d, J = 8.7 Hz, 2H, Ar-H), 7.28 (dd, J = 4.8, 3.1 Hz, 1H, Ar-H), 7.18 (s, 1H, Ar-H), 7.17 – 7.03 (m, 2H, Ar-H), 7.00 (t, J = 8.2 Hz, 4H, Ar-H), 4.27 (s, 2H, CH₂), 3.88 (s, 3H, OCH₃), 3.86 (s, 3H, OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 160.7 (C⁹), 160.5 (C⁹), 160.5 (C⁹), 157.3 (C⁹), 149.3 (C⁹), 140.0 (C⁹), 132.6 (C⁹), 131.3 (C⁹), 128.9 (CH), 128.5 (CH), 128.4 (CH), 125.6 (CH), 121.8 (CH), 118.3 (CH), 115.4 (CH), 114.5 (CH), 114.2 (CH), 55.5 (OCH₃), 55.5 (OCH₃), 39.7 (CH₂); HRMS (ESI): m/z calcd for C₂₄H₂₂NSO₂: 388.1371 [(M+H)]⁺; Found: 388.1372.

**6.4.7 Au-catalyzed hydroimination of terminal aryl alkynes 5**

General procedure: Complex LAuCl 1 (8mg, 5 mol%) and KB(C₆F₅)₄ (7 mg, 5 mol%) were introduced in a J-Young NMR tube. The C₆D₆ (0.5 mL), 1,3,5-trimethoxybenzene (0.1 mmol, 16.8 mg), the desired alkyne 5 (0.4 mmol) and imine 17 (0.2 mmol) were added in this reaction.
The reaction mixture was heated at 150 °C and monitored periodically by $^1$H NMR. Upon completion, the products were purified on triethylamine deactivated silica gel with the appropriate mixture of $n$-hexane and ethyl acetate.

18a: Yellow oil; 47% yield (isolated); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.01-7.96 (m, 2H, Ar-H), 7.82 (m, 2H, Ar-H), 7.51 (m, 3H, Ar-H), 7.41 (m, 5H, Ar-H), 7.31-7.28 (m, 3H, Ar-H), 6.86 (d, $J$ = 8.6 Hz, 1H, CH), 6.10 (d, $J$ = 8.6 Hz, 1H, CH); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 167.4 (N=C), 139.6 (C$q$), 136.8 (C$q$), 136.4 (CH), 136.2 (C$q$), 130.8 (CH), 130.6 (CH), 129.5 (CH), 129.0 (CH), 128.5 (CH), 128.3 (CH), 127.3 (CH), 125.5 (CH); HRMS (ESI): m/z calcd for C$_{21}$H$_{18}$N: 284.1439 [(M+H)$^+$]; found: 284.1437.

18a*: Yellow oil; 46% yield (isolated); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.95 (d, $J$ = 7.5 Hz, 2H, Ar-H), 7.84-7.75 (m, 2H, Ar-H), 7.52-7.34 (m, 8H, Ar-H), 7.28-7.25 (m, 3H, Ar-H), 6.83 (dd, $J$ = 164.5, 8.6 Hz, 1H, CH), 6.07 (dd, $J$ = 8.5, 1.5 Hz, 1H, CH); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 136.2 (C$q$); HRMS (ESI): m/z calcd for C$_{20}$H$_{18}$N: 285.1473 [(M+H)$^+$]; Found: 285.1478.

18b: Yellow oil; 50% yield (isolated); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.83 (d, $J$ = 8.5 Hz, 2H, Ar-H), 7.79-7.74 (m, 2H, Ar-H), 7.51-7.46 (m, 5H, Ar-H), 7.46-7.37 (m, 3H, Ar-H), 7.26 (m, 2H, Ar-H), 6.84 (d, $J$ = 8.5 Hz, 1H, CH), 6.00 (d, $J$ = 8.6 Hz, 1H, CH); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 168.0 (N=C), 139.4 (C$q$), 137.0 (CH), 136.1 (C$q$), 135.8, (C$q$) 132.3 (CH), 131.4 (CH), 130.8 (CH), 129.5 (CH), 129.2 (CH), 129.0 (CH), 128.6 (CH), 128.4 (CH), 124.2 (CH), 121.3 (C$q$); HRMS (ESI): m/z calcd for C$_{21}$H$_{17}$BrN: 362.0544 [(M+H)$^+$]; found: 362.0548.
18c: Yellow oil; 39% yield (isolated); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.89 (d, $J$ = 8.1 Hz, 2H, Ar-H), 7.82 (m, 2H, Ar-H), 7.54-7.47 (m, 3H, Ar-H), 7.47-7.38 (m, 3H, Ar-H), 7.29 (m, 2H, Ar-H), 7.22 (d, $J$ = 8.0 Hz, 2H, Ar-H), 6.82 (d, $J$ = 8.5 Hz, 1H, CH$_3$), 6.08 (d, $J$ = 8.5 Hz, 1H, CH$_3$), 2.40 (s, 3H, Ar-H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 166.8 (C$^\alpha$), 139.7 (C$^\alpha$), 137.2 (C$^\beta$), 136.3 (C$^\beta$), 135.6 (CH), 134.1 (C$^\gamma$), 130.8 (CH), 130.4 (CH), 129.4 (CH), 129.0 (CH), 129.0 (CH), 128.9 (CH), 128.5 (CH), 128.3 (CH), 125.7 (CH), 21.4 (CH$_3$); HRMS (ESI): m/z calcd for C$_{22}$H$_{20}$N: 298.1596 [(M+H)$^+$]; found: 298.1595.

18d: Yellow oil; 37% yield (isolated); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.94 (d, $J$ = 7.4 Hz, 2H, Ar-H), 7.75 (d, $J$ = 8.9 Hz, 2H, Ar-H), 7.35 (t, $J$ = 7.7 Hz, 2H, Ar-H), 7.25-7.18 (m, 3H, Ar-H), 6.99 (d, $J$ = 8.7 Hz, 2H, Ar-H), 6.91 (d, $J$ = 8.9 Hz, 2H, Ar-H), 6.84 (d, $J$ = 8.6 Hz, 1H, CH$_3$), 6.01 (d, $^3$J = 8.6 Hz, 1H, CH$_3$), 3.88 (s, 3H, OCH$_3$), 3.86 (s, 3H, OCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 166.9 (N=C), 161.7 (C$^\alpha$), 160.1 (C$^\alpha$), 137.2 (C$^\beta$), 136.9 (CH), 131.3 (CH), 130.8 (CH), 130.6 (CH), 128.5 (C$^\gamma$), 128.2 (CH), 126.9 (CH), 123.9 (CH), 113.8 (CH), 113.7 (CH), 55.5 (OCH$_3$), 55.4 (OCH$_3$); HRMS (ESI): m/z calcd for C$_{23}$H$_{22}$NO$_2$: 344.1651 [(M+H)$^+$]; found: 344.1649.

18e: Yellow oil; 44% yield (isolated); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.82 (d, $J$ = 8.5 Hz, 2H, Ar-H), 7.73 (d, $J$ = 8.9 Hz, 2H, Ar-H), 7.47 (d, $J$ = 8.5 Hz, 2H, Ar-H), 7.20 (d, $J$ = 8.6 Hz, 2H, Ar-H), 6.99 (d, $J$ = 8.6 Hz, 2H, Ar-H), 6.91 (d, $J$ = 8.9 Hz, 2H, Ar-H), 6.86 (d, $J$ = 8.6 Hz, 1H, CH$_3$), 5.93 (d, $J$ = 8.6 Hz, 1H, CH$_3$), 3.88 (s, 3H, OCH$_3$), 3.86 (s, 3H, OCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 167.4 (N=C), 161.9 (C$^\alpha$), 160.2 (C$^\alpha$), 137.6 (CH), 136.1 (C$^\alpha$), 132.7 (C$^\beta$), 132.1 (CH), 131.3 (CH), 131.3 (CH), 130.8 (CH), 128.3 (Cq), 122.6 (CH), 120.8 (C$^\gamma$), 113.8 (CH), 113.7 (CH), 55.5 (OCH$_3$), 55.5 (OCH$_3$); HRMS (ESI): m/z calcd for C$_{23}$H$_{21}$NO$_2$Br: 422.0756 [(M+H)$^+$]; found: 422.0752.

18f: Yellow oil; 37% yield (isolated); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.85 (d, $J$ = 8.1 Hz, 2H, Ar-H), 7.75 (d, $J$ = 8.9 Hz, 2H, Ar-H), 7.19 (m, 4H, Ar-H), 6.99 (d, $J$ = 8.7 Hz, 2H, Ar-H),
6.91 (d, J = 8.9 Hz, 2H, Ar-H), 6.81 (d, J = 8.6 Hz, 1H, CH), 5.99 (d, J = 8.6 Hz, 1H, CH), 3.88 (s, 3H, OCH$_3$), 3.86 (s, 3H, OCH$_3$), 2.37 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 166.3 (N=C), 161.6 (C$^\beta$), 160.0 (C$^\beta$), 160.0 (C$^\beta$), 136.1 (CH), 134.4 (C$^\beta$), 132.9 (C$^\beta$), 131.2 (CH), 130.8 (CH), 130.6 (CH), 129.0 (CH), 128.6 (C$^\beta$), 124.1 (CH), 113.8 (CH), 113.6 (CH), 55.5 (OCH$_3$), 55.4 (OCH$_3$), 21.4 (CH$_3$); HRMS (ESI): m/z calcd for C$_{24}$H$_{24}$rNO$_2$: 358.1807 [(M+H)$^+$]; found: 358.1809.

18g: Yellow oil; 47% yield (isolated); $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.91 (d, J = 7.5 Hz, 2H, Ar-H), 7.76 (dd, J = 8.8, 5.6 Hz, 2H, Ar-H), 7.37 (t, J = 7.7 Hz, 2H, Ar-H), 7.25 (dd, J = 7.4, 4.3 Hz, 3H, Ar-H), 7.19 (t, J = 8.6 Hz, 2H, Ar-H), 7.08 (t, J = 8.6 Hz, 2H, Ar-H), 6.77 (d, J = 8.6 Hz, 1H, CH), 6.09 (d, J = 8.6 Hz, 1H, CH); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 165.8 (d, J$_{CF}$ = 145.9 Hz, C$^\beta$), 165.1 (N=C), 163.3 (d, J$_{CF}$ = 143.1 Hz, C$^\beta$), 136.7 (C$^\beta$), 135.9 (CH), 135.8 (d, J$_{CF}$ = 2.8 Hz, C$^\beta$), 131.8 (d, J$_{CF}$ = 3.5 Hz, C$^\beta$), 131.4 (d, J$_{CF}$ = 8.4 Hz, CH), 131.1 (d, J$_{CF}$ = 8.4 Hz, CH), 130.8 (CH), 128.3 (CH), 127.4 (CH), 125.9 (CH), 116.0 (d, J$_{CF}$ = 21.4 Hz, CH), 115.6 (d, J$_{CF}$ = 21.6 Hz, CH); $^{19}$F NMR (376 MHz, CDCl$_3$): δ = −109.7 (m, 1F), −111.2 (m, 1F); HRMS (ESI): m/z calcd for C$_{21}$H$_{16}$NF$_2$: 320.1251 [(M+H)$^+$]; found: 320.1252.

18h: Yellow solid; 42% yield (isolated); Mp: 113 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ = 7.78 (d, J = 8.5 Hz, 2H, Ar-H), 7.73 (dd, J = 8.8, 5.6 Hz, 2H, Ar-H), 7.49 (d, J = 8.5 Hz, 2H, Ar-H), 7.28-7.17 (m, 4H, Ar-H), 7.08 (t, J = 8.6 Hz, 2H, Ar-H), 6.79 (d, J = 8.5 Hz, 1H, CH), 6.02 (d, J = 8.6 Hz, 1H, CH); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 165.9 (d, J$_{CF}$ = 148.6 Hz, C$^\beta$), 165.6 (N=C), 163.43 (d, J$_{CF}$ = 146.5 Hz, C$^\beta$), 136.5 (CH), 135.7 (d, J$_{CF}$ = 2.9 Hz, C$^\beta$), 135.6 (C$^\beta$), 132.2 (CH), 131.6 (d, J$_{CF}$ = 3.6 Hz, C$^\beta$), 131.5 (d, J$_{CF}$ = 9.3 Hz, CH), 131.4 (CH), 131.1 (d, J$_{CF}$ = 8.1 Hz, CH), 124.6 (CH), 121.4 (C$^\beta$), 116.0 (d, J$_{CF}$ = 21.2 Hz, CH), 115.6 (d, J$_{CF}$ = 21.7 Hz, CH); $^{19}$F NMR (376 MHz, CDCl$_3$): δ = −109.2 (m, 1F), −110.9 (m, 1F); HRMS (ESI): m/z calcd for C$_{21}$H$_{15}$NF$_2$Br: 398.0356 [(M+H)$^+$]; found: 398.0353.
18i: Yellow solid; 32% yield (isolated); Mp: 97 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.84 (d, $J = 8.1$ Hz, 2H, Ar-H), 7.81-7.73 (m, 2H, Ar-H), 7.28 (m, 2H, Ar-H), 7.24-7.17 (m, 4H, Ar-H), 7.10 (t, $J = 8.7$ Hz, 2H, Ar-H), 6.76 (d, $J = 8.5$ Hz, 1H, CH$_3$), 6.10 (d, $J = 8.5$ Hz, 1H, CH$_3$), 2.40 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 165.7 (d, $J_{C-F} = 143.1$ Hz, C$_q$), 164.5 (N=C), 163.2 (d, $J_{C-F} = 140.4$ Hz, C$_q$), 137.4 (C$_q$), 135.9 (d, $J_{C-F} = 3.0$ Hz, C$_q$), 135.2 (CH), 133.9 (C$_q$), 131.8 (d, $J_{C-F} = 3.6$ Hz, C$_q$), 131.4 (d, $J_{C-F} = 8.4$ Hz, CH), 130.7 (CH), 129.1 (CH), 126.1 (CH), 115.9 (d, $J_{C-F} = 21.4$ Hz, CH), 115.5 (d, $J_{C-F} = 21.5$ Hz, CH), 21.4 (CH$_3$); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = –109.9 (m), –111.3 (m); HRMS (ESI): m/z calcd for C$_{22}$H$_{18}$NF$_2$: 334.1407 [(M+H)$^+$]; found: 334.1411.

18j: Yellow oil; 47% yield (isolated); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.91 (d, $J = 7.5$ Hz, 2H, Ar-H), 7.56 (m, 2H, Ar-H), 7.45 (m, 3H, Ar-H), 7.34 (t, $J = 7.7$ Hz, 2H, Ar-H), 7.21 (t, $J = 7.4$ Hz, 1H, Ar-H), 6.76 (d, $J = 8.7$ Hz, 1H, CH$_3$), 5.81 (d, $J = 8.7$ Hz, 1H, CH$_3$), 4.03 (s, 3H, OCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 162.9 (N=C), 137.2 (C$_q$), 133.3 (CH), 131.3 (C$_q$), 130.6 (CH), 129.6 (CH), 129.2 (CH), 128.4 (CH), 128.2 (CH), 126.5 (CH), 119.8 (CH), 54.3 (OCH$_3$); HRMS (ESI): m/z calcd for C$_{16}$H$_{18}$NO: 238.1230 [(M+H)$^+$]; found: 238.1230.

18k: Yellow oil; 51% yield (isolated); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.79 (d, $J = 8.5$ Hz, 2H, Ar-H), 7.57-7.51 (m, 2H, Ar-H), 7.46 (m, 5H, Ar-H), 6.79 (d, $J = 8.6$ Hz, 1H, CH$_3$), 5.74 (d, $J = 8.6$ Hz, 1H, CH$_3$), 4.02 (s, 3H, OCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 163.5 (N=C), 136.2 (C$_q$), 134.0 (CH), 131.2 (CH), 131.1 (C$_q$), 131.1 (CH), 130.7 (CH), 129.2 (CH), 128.5 (CH), 120.2 (C$_q$), 118.5 (CH), 54.4 (OCH$_3$); HRMS (ESI): m/z calcd for C$_{16}$H$_{18}$NOBr: 316.0337 [(M+H)$^+$]; found: 316.0337.

18l: Yellow oil; 39% yield (isolated); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.82 (d, $J = 8.1$ Hz, 2H, Ar-H), 7.57 (m, 2H, Ar-H), 7.45 (m, 3H, Ar-H), 7.17 (d, $J = 8.0$ Hz, 2H, Ar-H), 6.73 (d, $J = 8.6$ Hz, 1H, CH$_3$), 5.80 (d, $J = 8.6$ Hz, 1H, CH$_3$), 4.04 (s, 3H, OCH$_3$), 2.37 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 162.6 (N=C), 136.2 (C$_q$), 134.4 (C$_q$), 132.4 (CH), 131.3 (C$_q$), 131.1 (CH), 130.7 (CH), 129.2 (CH), 128.5 (CH), 120.2 (C$_q$), 118.5 (CH), 54.4 (OCH$_3$); HRMS (ESI): m/z calcd for C$_{16}$H$_{18}$NOBr: 316.0337 [(M+H)$^+$]; found: 316.0337.
130.5 (CH), 129.5 (CH), 129.2 (CH), 128.9 (CH), 128.4 (CH), 119.8 (CH), 54.3 (OCH₃), 21.4 (CH₃); HRMS (ESI): m/z calcd for C17H18NO: 252.1388 [(M+H)]⁺; found: 252.1385.
6.4.7 $^1$H, $^{13}$C and $^{19}$F NMR Spectra

**Figure 6.16** $^1$H NMR spectrum of 2

**Figure 6.17** $^{13}$C NMR spectrum of 2
Figure 6.18 $^1$H NMR spectrum of 4

Figure 6.19 $^{13}$C NMR spectrum of 4
**Figure 6.20** $^{19}\text{F}$ NMR spectrum of 4

**Figure 6.21** $^1\text{H}$ NMR spectrum of 1
Figure 6.22 $^{13}$C NMR spectrum of 1

Figure 6.23 $^1$H NMR spectrum of 7a
Figure 6.24 $^{13}$C NMR spectrum of 7a

Figure 6.25 $^1$H NMR spectrum of 7a*
Figure 6.26 $^{13}$C NMR spectrum of 7a*

Figure 6.27 $^1$H NMR spectrum of 5b
Figure 6.28 $^{13}$C NMR spectrum of 5b

Figure 6.29 $^1$H NMR spectrum of 5c
Figure 6.30 $^{13}$C NMR spectrum of 5c

Figure 6.31 $^1$H NMR spectrum of 5d
Figure 6.32 $^{13}$C NMR spectrum of 5d

Figure 6.33 $^1$H NMR spectrum of 5e
Figure 6.34 $^{13}$C NMR spectrum of 5e

Figure 6.35 $^1$H NMR spectrum of 5f
Figure 6.36 $^{13}$C NMR spectrum of 5f

Figure 6.37 $^{19}$F NMR spectrum of 5f
Figure 6.38 $^1$H NMR spectrum of $5g$

Figure 6.39 $^{13}$C NMR spectrum of $5g$
Figure 6.40 $^{19}$F NMR spectrum of 5g

Figure 6.41 $^1$H NMR spectrum of 5h
Figure 6.42 $^{13}$C NMR spectrum of 5h

Figure 6.43 $^{19}$F NMR spectrum of 5h
Figure 6.44 $^1$H NMR spectrum of 5i

Figure 6.45 $^{13}$C NMR spectrum of 5i
*Figure 6.46* $^1$H NMR spectrum of 5j

*Figure 6.47* $^{13}$C NMR spectrum of 5j
Figure 6.48 $^1$H NMR spectrum of 5k

Figure 6.49 $^{13}$C NMR spectrum of 5k
Figure 6.50 $^1$H NMR spectrum of 51

Figure 6.51 $^{13}$C NMR spectrum of 51
Figure 6.52 $^1$H NMR spectrum of $5m$

Figure 6.53 $^{13}$C NMR spectrum of $5m$
Figure 6.54 $^1$H NMR spectrum of 16a

Figure 6.55 $^{13}$C NMR spectrum of 16a
Figure 6.56 $^{19}$F NMR spectrum of 16a

Figure 6.57 $^1$H NMR spectrum of 16b
Figure 6.58 $^{13}$C NMR spectrum of 16b

Figure 6.59 $^1$H NMR spectrum of 16c
Figure 6.60 $^{13}$C NMR spectrum of 16c

Figure 6.61 $^{19}$F NMR spectrum of 16c
Figure 6.62 $^1$H NMR spectrum of 16d

Figure 6.63 $^{13}$C NMR spectrum of 16d
Figure 6.64 $^{19}$F NMR spectrum of 16d

Figure 6.65 $^1$H NMR spectrum of 16e
Figure 6.66 $^{13}$C NMR spectrum of 16e

Figure 6.67 $^1$H NMR spectrum of 18a
Figure 6.68 $^{13}$C NMR spectrum of 18a

Figure 6.69 $^1$H NMR spectrum of 18a*
Figure 6.70 $^{13}$C NMR spectrum of 18a

Figure 6.71 $^1$H NMR spectrum of 18b
Figure 6.72 $^{13}$C NMR spectrum of 18b

Figure 6.73 $^1$H NMR spectrum of 18c
Figure 6.74 $^{13}$C NMR spectrum of 18c

Figure 6.75 $^1$H NMR spectrum of 18d
**Figure 6.76** $^{13}$C NMR spectrum of 18d

**Figure 6.77** $^1$H NMR spectrum of 18e
Figure 6.78 $^{13}$C NMR spectrum of $18\text{e}$

Figure 6.79 $^1$H NMR spectrum of $18\text{f}$
Figure 6.80 $^{13}$C NMR spectrum of $18\text{g}$

Figure 6.81 $^1$H NMR spectrum of $18\text{g}$
Figure 6.82 $^{13}$C NMR spectrum of $18g$

Figure 6.83 $^{19}$F NMR spectrum of $18g$
Figure 6.84 $^1$H NMR spectrum of 18h

Figure 6.85 $^{13}$C NMR spectrum of 18h
Figure 6.86 $^{19}$F NMR spectrum of $18h$

Figure 6.87 $^1$H NMR spectrum of $18i$
Figure 6.88 $^{13}$C NMR spectrum of 18i

Figure 6.89 $^{19}$F NMR spectrum of 18i
Figure 6.90 $^1$H NMR spectrum of \textbf{18j}

Figure 6.91 $^{13}$C NMR spectrum of \textbf{18j}
Figure 6.92 $^1$H NMR spectrum of 18k

Figure 6.93 $^{13}$C NMR spectrum of 18k
Figure 6.94 ¹H NMR spectrum of 18l

Figure 6.95 ¹³C NMR spectrum of 18l
6.5 Reference


Conclusion

As mentioned in Chapter 1, the aim of the project is to investigate the synthesis and reactivities of novel Group 14 divalent species such as carbene and germylene. First, we have developed a cyclic (alkyl)(amino) germylene (CAAGe) in Chapter 2. CAAGe possesses the high-lying HOMO−1 and low-lying LUMO, which was supported by DFT calculations.

In Chapter 3, we have investigated the reactivity of CAAGe with S₈ and N₂O. The oxidation reaction of CAAGe by S₈ led to the formation of the sulfido-bridged dimers as a mixture of two diastereomers involving Ge₂S₂ four-membered ring framework. In contrast, when CAAGe was oxidized by N₂O, and only trans product containing the Ge₂O₂ four-membered ring skeleton was obtained. The reaction of CAAGe with TEMPO led to the formation of a 1:2 adduct.

In Chapter 4, a modified CAAGe with an adamantyl group on the N atom was developed. In the reaction of CAAGe with hydrosilanes in the presence of 20 mol% B(C₆F₅)₃, CAAGe was transformed into germynes 10 and 11 via silyl group exchange. The corresponding kinetic studies have been performed to support the mechanism proposed.

In Chapter 5, the reactions of CAAGe with various gold(I), palladium(0) and palladium(II) complexes have been examined in Chapter 5. The Au−Cl bond insertion products [ClGe−Au−PPh₃] and [ClGe−Au−NHC] were formed in the reactions of CAAGe with triphenylphosphine gold(I) chloride and NHC gold(I) chloride respectively. The reactions of [ClGe−Au−NHC] with various silver reagents afforded the corresponding [Ge−Au−NHC]•X complex. Furthermore, the reaction of CAAGe with Pd(PPh₃)₄ resulted in the formation of germylene bis(triphenylphosphine) palladium(0), which was also formed by the reaction of CAAGe with Pd(PPh₃)₂Cl₂.

Lastly, a new gold(I) complex featuring a pyrid-2-ylidene ligand was synthesized and fully characterized. Gold(I) complex has been employed in hydroamination of alkynes with ammonia, which provided an efficient synthetic method for the construction of pyridine derivatives. Gold(I)
complex has also been utilized in the hydroimination of alkynes with imines, which indicated an apparent anti-Markovnikov regioselectivity to form 2-aza-1,3-dienes. A plausible mechanism involving both Markovnikov and Anti-Markovnikov addition was proposed and certified by the experimental studies.
List of Publications


Appendix A Crystallographic details

X-ray data collection and structural refinement. Intensity data for all compounds were collected using a Bruker APEX II diffractometer. The structure was solved by direct phase determination (SHELX-2013) and refined for all data by full-matrix least-squares methods on F2. All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations.
**Chapter 2 Supplementary table | X-ray data for 3, 4 and 1.**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>3</th>
<th>4</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{21}$H$</em>{37}$NSi$_2$</td>
<td>C$<em>{21}$H$</em>{37}$Cl$_2$GeNSi$_2$</td>
<td>C$<em>{21}$H$</em>{37}$GeNSi$_2$</td>
</tr>
<tr>
<td>Fw</td>
<td>359.69</td>
<td>503.18</td>
<td>432.28</td>
</tr>
<tr>
<td>Cryst syst</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 1 21/c 1</td>
<td>P 1 21/n 1</td>
<td>P n m a</td>
</tr>
<tr>
<td>Size (mm$^3$)</td>
<td>0.180 x 0.220 x 0.360</td>
<td>0.260 x 0.300 x 0.320</td>
<td>0.220 x 0.300 x 0.420</td>
</tr>
<tr>
<td>T/K</td>
<td>103(2)</td>
<td>103(2)</td>
<td>103(2)</td>
</tr>
<tr>
<td>a, Å</td>
<td>12.2230(12)</td>
<td>17.7322(15)</td>
<td>18.4853(11)</td>
</tr>
<tr>
<td>b, Å</td>
<td>12.3881(14)</td>
<td>7.2799(6)</td>
<td>10.4296(6)</td>
</tr>
<tr>
<td>c, Å</td>
<td>15.7504(16)</td>
<td>20.5722(17)</td>
<td>12.7509(8)</td>
</tr>
<tr>
<td>α, deg</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β, deg</td>
<td>102.165(3)</td>
<td>104.674(3)</td>
<td>90</td>
</tr>
<tr>
<td>γ, deg</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V, Å$^3$</td>
<td>2331.4(4)</td>
<td>2569.0(4)</td>
<td>2458.3(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>d calc g·cm$^{-3}$</td>
<td>1.025</td>
<td>1.301</td>
<td>1.168</td>
</tr>
<tr>
<td>μ, mm$^{-1}$</td>
<td>0.155</td>
<td>1.501</td>
<td>1.348</td>
</tr>
<tr>
<td>Refl collected</td>
<td>31602</td>
<td>33105</td>
<td>18278</td>
</tr>
<tr>
<td>T$<em>{max}$ / T$</em>{min}$</td>
<td>0.9730/0.9460</td>
<td>0.6960/0.6450</td>
<td>0.7560/0.6010</td>
</tr>
<tr>
<td>N$_{meas}$</td>
<td>6254</td>
<td>8173</td>
<td>2656</td>
</tr>
<tr>
<td>[R int]</td>
<td>0.0749</td>
<td>0.0690</td>
<td>0.1358</td>
</tr>
<tr>
<td>R [I&gt;2sigma(I)]</td>
<td>0.0448</td>
<td>0.0521</td>
<td>0.0629</td>
</tr>
<tr>
<td>R$_w$ [I&gt;2sigma(I)]</td>
<td>0.1044</td>
<td>0.1085</td>
<td>0.1149</td>
</tr>
<tr>
<td>GOF</td>
<td>1.033</td>
<td>1.154</td>
<td>1.030</td>
</tr>
<tr>
<td>Largest diff. peak/ hole[e. Å$^3$]</td>
<td>0.362/ -0.236</td>
<td>1.283/-0.729</td>
<td>0.295/ -0.575</td>
</tr>
</tbody>
</table>
### Chapter 3 Supplementary table | X-ray data for 2a, 2b, 3, 4 and 5.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>2a</th>
<th>2b</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$C_{42}H_{75}Ge_2N_2S_2Si_4$</td>
<td>$C_{42}H_{75}Ge_2N_2S_2Si_4$</td>
<td>$C_{21}H_{38}Cl_GaGeNSi_2$</td>
</tr>
<tr>
<td>Fw</td>
<td>929.70</td>
<td>928.69</td>
<td>644.81</td>
</tr>
<tr>
<td>Cryst syst</td>
<td>monoclinic</td>
<td>triclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 1 21/n 1</td>
<td>P - 1</td>
<td>P 1 21/c 1</td>
</tr>
<tr>
<td>Size (mm$^3$)</td>
<td>0.220 x 0.300 x 0.420</td>
<td>0.200 x 0.240 x 0.420</td>
<td>0.020 x 0.080 x 0.140</td>
</tr>
<tr>
<td>T/K</td>
<td>103(2)</td>
<td>103(2)</td>
<td>103(2)</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>10.2311(6)</td>
<td>10.489(4)</td>
<td>11.8503(2)</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>26.3317(18)</td>
<td>11.566(4)</td>
<td>17.4160(3)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>18.5201(13)</td>
<td>12.544(5)</td>
<td>14.7239(3)</td>
</tr>
<tr>
<td>$a$, deg</td>
<td>90</td>
<td>105.736(8)</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$, deg</td>
<td>91.640(2)</td>
<td>106.806(7)</td>
<td>107.3473(9)</td>
</tr>
<tr>
<td>$\gamma$, deg</td>
<td>90</td>
<td>111.124(7)</td>
<td>90</td>
</tr>
<tr>
<td>V, Å$^3$</td>
<td>4987.3(6)</td>
<td>1233.0(8)</td>
<td>2900.57(9)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>$d_{calc}$: g·cm$^{-3}$</td>
<td>1.238</td>
<td>1.251</td>
<td>1.477</td>
</tr>
<tr>
<td>$\mu$, mm$^{-1}$</td>
<td>1.414</td>
<td>1.430</td>
<td>6.670</td>
</tr>
<tr>
<td>Refl collected</td>
<td>75028</td>
<td>4359</td>
<td>23363</td>
</tr>
<tr>
<td>$T_{max}$/$T_{min}$</td>
<td>0.7460/ 0.5880</td>
<td>0.7630/ 0.5850</td>
<td>0.8780/ 0.4550</td>
</tr>
<tr>
<td>$N_{meas}$</td>
<td>15294</td>
<td>6915</td>
<td>5110</td>
</tr>
<tr>
<td>[R int]</td>
<td>0.1900</td>
<td>0.1031</td>
<td>0.0487</td>
</tr>
<tr>
<td>R [I&gt;2sigma(I)]</td>
<td>0.0729</td>
<td>0.1238</td>
<td>0.0410</td>
</tr>
<tr>
<td>$R_w$ [I&gt;2sigma(I)]</td>
<td>0.1484</td>
<td>0.2585</td>
<td>0.1111</td>
</tr>
<tr>
<td>GOF</td>
<td>0.991</td>
<td>1.074</td>
<td>1.093</td>
</tr>
<tr>
<td>Largest diff. peak/ hole[e. Å$^{-3}$]</td>
<td>2.128/-1.539</td>
<td>1.336/-0.450</td>
<td>0.835/-0.894</td>
</tr>
<tr>
<td>Compounds</td>
<td>4</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>Formula</td>
<td>C(<em>{39})H(</em>{73})GeN(_3)O(_2)Si(_2)</td>
<td>C(<em>{21})H(</em>{37})GeNOSi(_2)</td>
<td></td>
</tr>
<tr>
<td>Fw</td>
<td>744.77</td>
<td>448.28</td>
<td></td>
</tr>
<tr>
<td>Crystsyst</td>
<td>triclinic</td>
<td>triclinic</td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>P -1</td>
<td>P -1</td>
<td></td>
</tr>
<tr>
<td>Size (mm(^3))</td>
<td>0.060 x 0.200 x 0.400</td>
<td>0.380 x 0.400 x 0.420</td>
<td></td>
</tr>
<tr>
<td>T/K</td>
<td>103(2)</td>
<td>103(2)</td>
<td></td>
</tr>
<tr>
<td>a, Å</td>
<td>12.027(3)</td>
<td>10.1766(6)</td>
<td></td>
</tr>
<tr>
<td>b, Å</td>
<td>17.639(4)</td>
<td>12.0888(7)</td>
<td></td>
</tr>
<tr>
<td>c, Å</td>
<td>19.606(4)</td>
<td>21.8730(14)</td>
<td></td>
</tr>
<tr>
<td>a, deg</td>
<td>98.477(2)</td>
<td>80.3144(18)</td>
<td></td>
</tr>
<tr>
<td>β, deg</td>
<td>92.2855(19)</td>
<td>80.8124(18)</td>
<td></td>
</tr>
<tr>
<td>γ, deg</td>
<td>90.304(2)</td>
<td>65.2397(18)</td>
<td></td>
</tr>
<tr>
<td>V, Å(^3)</td>
<td>4110.3(15)</td>
<td>2396.7(3)</td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>(d_{\text{calc}}), g·cm(^{-3})</td>
<td>1.204</td>
<td>1.242</td>
<td></td>
</tr>
<tr>
<td>(μ), mm(^{-1})</td>
<td>0.839</td>
<td>1.388</td>
<td></td>
</tr>
<tr>
<td>Refl collected</td>
<td>19943</td>
<td>96838</td>
<td></td>
</tr>
<tr>
<td>(T_{\text{max}}/ T_{\text{min}})</td>
<td>0.9510/ 0.7300</td>
<td>0.6210/ 0.5930</td>
<td></td>
</tr>
<tr>
<td>(N_{\text{meas}})</td>
<td>19943</td>
<td>21165</td>
<td></td>
</tr>
<tr>
<td>[R int]</td>
<td>0.1425</td>
<td>0.1588</td>
<td></td>
</tr>
<tr>
<td>R [I&gt;2(σ(I))]</td>
<td>0.0719</td>
<td>0.0606</td>
<td></td>
</tr>
<tr>
<td>R(_{w}) [I&gt;2(σ(I))]</td>
<td>0.1366</td>
<td>0.1240</td>
<td></td>
</tr>
<tr>
<td>GOF</td>
<td>0.919</td>
<td>0.998</td>
<td></td>
</tr>
<tr>
<td>Largest diff. peak/ hole[e. Å(^{-1})]</td>
<td>0.726/ -1.116</td>
<td>0.819/ -0.896</td>
<td></td>
</tr>
</tbody>
</table>
### Supplementary Table

<table>
<thead>
<tr>
<th>Compounds</th>
<th>7</th>
<th>10</th>
<th>12b</th>
<th>12d</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C$<em>{19}$H$</em>{35}$GeNSi$_2$</td>
<td>C$<em>{37}$H$</em>{39}$GeNSi$_2$</td>
<td>C$<em>{34}$H$</em>{51}$GeNSe$_2$Si$_2$</td>
<td>C$<em>{46}$H$</em>{51}$GeNSe$_2$Si$_2$</td>
</tr>
<tr>
<td><strong>Fw</strong></td>
<td>406.25</td>
<td>626.46</td>
<td>760.44</td>
<td>904.56</td>
</tr>
<tr>
<td><strong>Crystsyst</strong></td>
<td>monoclinic</td>
<td>triclinic</td>
<td>triclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P 1 21/m 1</td>
<td>P - 1</td>
<td>P - 1</td>
<td>P 1 21/n 1</td>
</tr>
<tr>
<td><strong>Size (mm$^3$)</strong></td>
<td>0.100 x 0.120 x 0.320</td>
<td>0.100 x 0.140 x 0.160</td>
<td>0.120 x 0.220 x 0.240</td>
<td>0.080 x 0.200 x 0.220</td>
</tr>
<tr>
<td><strong>T/K</strong></td>
<td>153(2) K</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td><strong>a, Å</strong></td>
<td>6.81090(10)</td>
<td>10.8487(4)</td>
<td>10.0277(5)</td>
<td>17.0042(16)</td>
</tr>
<tr>
<td><strong>b, Å</strong></td>
<td>39.6790(8)</td>
<td>11.8926(6)</td>
<td>11.6736(6)</td>
<td>13.6366(13)</td>
</tr>
<tr>
<td><strong>c, Å</strong></td>
<td>12.4192(2)</td>
<td>13.2375(6)</td>
<td>16.9271(9)</td>
<td>18.009(2)</td>
</tr>
<tr>
<td><strong>α, deg</strong></td>
<td>90</td>
<td>94.4802(19)</td>
<td>75.9599(16)</td>
<td>90</td>
</tr>
<tr>
<td><strong>β, deg</strong></td>
<td>104.2011(7)</td>
<td>111.5290(17)</td>
<td>86.3631(17)</td>
<td>103.789(4)</td>
</tr>
<tr>
<td><strong>γ, deg</strong></td>
<td>90</td>
<td>90.9025(16)</td>
<td>65.3770(15)</td>
<td>90</td>
</tr>
<tr>
<td><strong>V, Å$^3$</strong></td>
<td>3253.72(10)</td>
<td>1582.06(12)</td>
<td>1745.89(16)</td>
<td>4055.6(7)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>6</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td><strong>d$_{calc}$ g· cm$^{-3}$</strong></td>
<td>1.244</td>
<td>1.315</td>
<td>1.447</td>
<td>1.481</td>
</tr>
<tr>
<td><strong>μ, mm$^{-1}$</strong></td>
<td>2.957</td>
<td>1.071</td>
<td>3.054</td>
<td>2.643</td>
</tr>
<tr>
<td><strong>Refl collected</strong></td>
<td>16556</td>
<td>24268</td>
<td>74683</td>
<td>8859</td>
</tr>
<tr>
<td><strong>T$<em>{max}$/T$</em>{min}$</strong></td>
<td>0.7560/0.4510</td>
<td>0.9000/0.8470</td>
<td>0.7110/0.5280</td>
<td>0.8160/0.5940</td>
</tr>
<tr>
<td><strong>N$_{meas}$</strong></td>
<td>5683</td>
<td>7910</td>
<td>9818</td>
<td>8859</td>
</tr>
<tr>
<td><strong>[R int]</strong></td>
<td>0.0454</td>
<td>0.0580</td>
<td>0.0994</td>
<td>0.0892</td>
</tr>
<tr>
<td><strong>R [I&gt;2sigma(I)]</strong></td>
<td>0.0594</td>
<td>0.0477</td>
<td>0.0543</td>
<td>0.0669</td>
</tr>
<tr>
<td><strong>R$_{w}$ [I&gt;2sigma(I)]</strong></td>
<td>0.1831</td>
<td>0.1040</td>
<td>0.1141</td>
<td>0.1594</td>
</tr>
<tr>
<td><strong>GOF</strong></td>
<td>1.147</td>
<td>0.997</td>
<td>1.119</td>
<td>1.062</td>
</tr>
<tr>
<td><strong>Largest diff. peak/hole [e. Å$^3$]</strong></td>
<td>1.499/-0.882</td>
<td>1.415/-0.497</td>
<td>1.445/-1.449</td>
<td>1.590/-1.220</td>
</tr>
</tbody>
</table>


Chapter 5 Supplementary table  | X-ray data for 3a, 3b, 4a, 4b, 5d and 6.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>3a</th>
<th>3b</th>
<th>4a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C39H52AuClGeNPSi2</td>
<td>C37H50AuClGeNPSi2</td>
<td>C48H73AuClGeN3Si2</td>
</tr>
<tr>
<td>Fw</td>
<td>926.97</td>
<td>900.93</td>
<td>1053.28</td>
</tr>
<tr>
<td>Cryst syst</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C 1 2/c 1</td>
<td>P 1 21/c 1</td>
<td>P 1 21/c 1</td>
</tr>
<tr>
<td>Size (mm³)</td>
<td>0.040 x 0.240 x</td>
<td>0.080 x 0.120 x</td>
<td>0.060 x 0.200 x</td>
</tr>
<tr>
<td>T/K</td>
<td>133(2) K</td>
<td>100(2)</td>
<td>103(2)</td>
</tr>
<tr>
<td>a, Å</td>
<td>17.7016(3)</td>
<td>12.8142(3)</td>
<td>18.0057(3)</td>
</tr>
<tr>
<td>b, Å</td>
<td>15.5137(3)</td>
<td>22.1010(5)</td>
<td>12.7387(2)</td>
</tr>
<tr>
<td>c, Å</td>
<td>29.9298(5)</td>
<td>14.3320(3)</td>
<td>22.8121(4)</td>
</tr>
<tr>
<td>α, deg</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β, deg</td>
<td>100.4377(9)</td>
<td>113.2443(10)</td>
<td>107.8530(9)</td>
</tr>
<tr>
<td>γ, deg</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V, Å³</td>
<td>8083.2(2)</td>
<td>3729.46(15)</td>
<td>4980.43(15)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>d calc g·cm⁻³</td>
<td>1.523</td>
<td>1.605</td>
<td>1.405</td>
</tr>
<tr>
<td>μ, mm⁻¹</td>
<td>9.389</td>
<td>4.941</td>
<td>7.401</td>
</tr>
<tr>
<td>Refl collected</td>
<td>33896</td>
<td>52235</td>
<td>33537</td>
</tr>
<tr>
<td>Tmax/ Tmin</td>
<td>0.7050/ 0.1430</td>
<td>0.6930/ 0.3010</td>
<td>0.6650/ 0.2150</td>
</tr>
<tr>
<td>Nmeasd</td>
<td>6968</td>
<td>8153</td>
<td>8840</td>
</tr>
<tr>
<td>[R int]</td>
<td>0.0477</td>
<td>0.0782</td>
<td>0.0481</td>
</tr>
<tr>
<td>R</td>
<td>0.0306</td>
<td>0.0369</td>
<td>0.0391</td>
</tr>
<tr>
<td>Rw</td>
<td>0.0786</td>
<td>0.0663</td>
<td>0.1080</td>
</tr>
<tr>
<td>GOF</td>
<td>1.158</td>
<td>1.050</td>
<td>1.077</td>
</tr>
<tr>
<td>Largest diff. peak/ hole[e. Å⁻³]</td>
<td>1.068/ -1.126</td>
<td>1.275/ -1.364</td>
<td>1.863/ -2.231</td>
</tr>
<tr>
<td>Compounds</td>
<td>4b</td>
<td>5d</td>
<td>6</td>
</tr>
<tr>
<td>-----------</td>
<td>----</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>Formula</td>
<td>( \text{C}<em>{47}\text{H}</em>{73}\text{AuCl}<em>{3}\text{GeN}</em>{3}\text{Si}_{2} )</td>
<td>( \text{C}<em>{64}\text{H}</em>{73}\text{AlAuF}<em>{36}\text{GeN}</em>{3}\text{O}<em>{4}\text{Si}</em>{2} )</td>
<td>( \text{C}<em>{57}\text{H}</em>{67}\text{GeNP}<em>{2}\text{PdSi}</em>{2} )</td>
</tr>
<tr>
<td>Fw</td>
<td>1112.17</td>
<td>1984.97</td>
<td>1063.22</td>
</tr>
<tr>
<td>Crystsyst</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>( \text{P} , 1 , 21/n , 1 )</td>
<td>( \text{P} , 1 , 21/c , 1 )</td>
<td>( \text{P} , -1 )</td>
</tr>
<tr>
<td>Size (mm(^3))</td>
<td>0.040 x 0.240 x 0.320</td>
<td>0.080 x 0.300 x 0.420</td>
<td>0.060 x 0.300 x 0.320</td>
</tr>
<tr>
<td>T/K</td>
<td>143(2)</td>
<td>103(2)</td>
<td>103(2)</td>
</tr>
<tr>
<td>( a, ) Å</td>
<td>18.6200(2)</td>
<td>10.7385(5)</td>
<td>12.181(2)</td>
</tr>
<tr>
<td>( b, ) Å</td>
<td>12.5818(2)</td>
<td>20.1534(9)</td>
<td>13.762(3)</td>
</tr>
<tr>
<td>( c, ) Å</td>
<td>23.5793(3)</td>
<td>36.3744(16)</td>
<td>17.215(3)</td>
</tr>
<tr>
<td>( \alpha, ) deg</td>
<td>90</td>
<td>90</td>
<td>95.183(3)</td>
</tr>
<tr>
<td>( \beta, ) deg</td>
<td>113.0519(7)</td>
<td>90.5836(18)</td>
<td>101.208(3)</td>
</tr>
<tr>
<td>( \gamma, ) deg</td>
<td>90</td>
<td>90</td>
<td>105.736(2)</td>
</tr>
<tr>
<td>( V, ) Å(^3)</td>
<td>5082.91(12)</td>
<td>7871.6(6)</td>
<td>2693.2(9)</td>
</tr>
<tr>
<td>( Z )</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>( d_{\text{calc}} ) g·cm(^{-3})</td>
<td>1.453</td>
<td>1.675</td>
<td>1.311</td>
</tr>
<tr>
<td>( \mu, ) mm(^{-1})</td>
<td>8.227</td>
<td>2.416</td>
<td>1.032</td>
</tr>
<tr>
<td>Refl collected</td>
<td>49255</td>
<td>96044</td>
<td>13297</td>
</tr>
<tr>
<td>( T_{\text{max}}/T_{\text{min}} )</td>
<td>0.7340/0.1780</td>
<td>0.8300/0.4300</td>
<td>0.9410/0.7340</td>
</tr>
<tr>
<td>( N_{\text{meas}} )</td>
<td>8949</td>
<td>20415</td>
<td>13297</td>
</tr>
<tr>
<td>([\text{R int}])</td>
<td>0.0662</td>
<td>0.0766</td>
<td>0</td>
</tr>
<tr>
<td>( R [|&gt;2\sigma(I)] )</td>
<td>0.0350</td>
<td>0.0618</td>
<td>0.0719</td>
</tr>
<tr>
<td>( R_w [|&gt;2\sigma(I)] )</td>
<td>0.0913</td>
<td>0.1464</td>
<td>0.1593</td>
</tr>
<tr>
<td>GOF</td>
<td>1.035</td>
<td>1.042</td>
<td>0.955</td>
</tr>
<tr>
<td>Largest diff. peak/ hole[e. Å(^{-3})]</td>
<td>2.080/ -0.991</td>
<td>2.468/ -1.404</td>
<td>1.060/ -1.214</td>
</tr>
</tbody>
</table>
**Chapter 6 Supplementary table**  | X-ray data for 1, 7b, 7g, 16d, 18h and 18i.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>1</th>
<th>7b</th>
<th>7g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C43H57AuCl3N</td>
<td>C24H16Br3N</td>
<td>C24H16F3N</td>
</tr>
<tr>
<td>Fw</td>
<td>891.21</td>
<td>558.11</td>
<td>376.38</td>
</tr>
<tr>
<td>Crystals</td>
<td>monoclinic</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 1 21/c 1</td>
<td>P -1</td>
<td>P 1</td>
</tr>
<tr>
<td>Size (mm$^3$)</td>
<td>0.040 x 0.160 x 0.220</td>
<td>0.080 x 0.240 x 0.280</td>
<td>0.010 x 0.040 x 0.120</td>
</tr>
<tr>
<td>T/K</td>
<td>103(2)</td>
<td>103(2)</td>
<td>103(2)</td>
</tr>
<tr>
<td>a, Å</td>
<td>20.7969(9)</td>
<td>9.8400(9)</td>
<td>11.219(5)</td>
</tr>
<tr>
<td>b, Å</td>
<td>9.1006(3)</td>
<td>13.6565(13)</td>
<td>11.500(6)</td>
</tr>
<tr>
<td>c, Å</td>
<td>22.4423(10)</td>
<td>15.8730(16)</td>
<td>14.861(8)</td>
</tr>
<tr>
<td>α, deg</td>
<td>90</td>
<td>102.909(6)</td>
<td>72.70(3)</td>
</tr>
<tr>
<td>β, deg</td>
<td>104.9810(10)</td>
<td>93.588(6)</td>
<td>89.67(3)</td>
</tr>
<tr>
<td>γ, deg</td>
<td>90</td>
<td>95.664(6)</td>
<td>77.32(3)</td>
</tr>
<tr>
<td>V, Å$^3$</td>
<td>4103.2(3)</td>
<td>2061.1(3)</td>
<td>1967.1(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>d calcd g·cm$^{-3}$</td>
<td>1.443</td>
<td>1.799</td>
<td>1.399</td>
</tr>
<tr>
<td>μ, mm$^{-1}$</td>
<td>3.810</td>
<td>5.882</td>
<td>0.103</td>
</tr>
<tr>
<td>Refl collected</td>
<td>37965</td>
<td>40100</td>
<td>31706</td>
</tr>
<tr>
<td>T max/ T min</td>
<td>0.8600 / 0.5600</td>
<td>0.6500 / 0.2900</td>
<td>0.9990 / 0.9880</td>
</tr>
<tr>
<td>N measd</td>
<td>10022</td>
<td>8099</td>
<td>14351</td>
</tr>
<tr>
<td>[R int]</td>
<td>0.0520</td>
<td>0.1300</td>
<td>0.1447</td>
</tr>
<tr>
<td>R [I&gt;2sigma(I)]</td>
<td>0.0350</td>
<td>0.0613</td>
<td>0.0782</td>
</tr>
<tr>
<td>R w [I&gt;2sigma(I)]</td>
<td>0.1129</td>
<td>0.1927</td>
<td>0.2260</td>
</tr>
<tr>
<td>GOF</td>
<td>1.158</td>
<td>1.032</td>
<td>0.957</td>
</tr>
<tr>
<td>Largest diff. peak/ hole[e. Å$^{-3}$]</td>
<td>1.564 / -1.541</td>
<td>2.803 / -1.027</td>
<td>0.787 / -0.440</td>
</tr>
<tr>
<td>Compounds</td>
<td>Formula</td>
<td>Fw</td>
<td>Crystyst</td>
</tr>
<tr>
<td>-----------</td>
<td>---------</td>
<td>----</td>
<td>----------</td>
</tr>
<tr>
<td>16d</td>
<td>C$<em>{27}$H$</em>{22}$F$_3$NO$_2$</td>
<td>449.45</td>
<td>monoclinic</td>
</tr>
<tr>
<td>18h</td>
<td>C$<em>{21}$H$</em>{14}$BrF$_2$N</td>
<td>398.24</td>
<td>monoclinic</td>
</tr>
<tr>
<td>18i</td>
<td>C$<em>{22}$H$</em>{17}$F$_2$N</td>
<td>333.36</td>
<td>triclinic</td>
</tr>
</tbody>
</table>

**Supplementary reference**

Appendix B Theoretical calculation

Gaussian 09 was used for all density functional theory (DFT) calculations.\textsuperscript{1} Geometry optimization and frequency calculations were performed using the level of theory as stated in each chapter. Specific details for the DFT calculations for each chapter are stated as follow:

Chapter 2

Geometry optimization, frequency calculations, natural bond orbital (NBO) analysis of compound \textbf{I} were performed at the B3LYP/6-311G(d,p) level of theory. Geometry optimization and frequency calculations for \textbf{VIII'\textquotesingle, IX'\textquotesingle, XI'\textquotesingle and I'\textquotesingle} were performed at the B3LYP/6-311G(d,p) level of theory.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
     & \textbf{C} & \textbf{N} & \textbf{Ge} \\
\hline
\textbf{VIII'\textquotesingle} & 0.74302498 & 1.27078519 & 0.000000048 \\
& -1.61271022 & -0.28435381 & 0.0000000049 \\
\textbf{IX'\textquotesingle} & 1.05725558 & 0.11946059 & 0.11946059 \\
\hline
\textbf{I'\textquotesingle} & -0.01946194 & 0.18178240 & 0.18178240 \\
\textbf{XI'\textquotesingle} & -0.01946194 & -0.01946194 & -0.01946194 \\
\hline
\end{tabular}
\end{table}
<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.27987150</td>
<td>-2.39347663</td>
<td>-0.37575975</td>
</tr>
<tr>
<td>H</td>
<td>0.86702911</td>
<td>-1.83483303</td>
<td>1.25662167</td>
</tr>
<tr>
<td>H</td>
<td>-1.2798736</td>
<td>-2.39347566</td>
<td>0.37575903</td>
</tr>
<tr>
<td>H</td>
<td>-0.86702818</td>
<td>-1.83483292</td>
<td>-1.25662180</td>
</tr>
<tr>
<td>H</td>
<td>3.22979845</td>
<td>-0.75885342</td>
<td>-0.75335152</td>
</tr>
<tr>
<td>H</td>
<td>2.98843889</td>
<td>0.91086252</td>
<td>-0.21056523</td>
</tr>
<tr>
<td>H</td>
<td>3.08799469</td>
<td>-0.39982450</td>
<td>0.97864251</td>
</tr>
<tr>
<td>H</td>
<td>-2.98843790</td>
<td>0.91086652</td>
<td>0.21055087</td>
</tr>
<tr>
<td>H</td>
<td>-3.08799908</td>
<td>-0.39983931</td>
<td>-0.97863532</td>
</tr>
<tr>
<td>H</td>
<td>-3.22979727</td>
<td>-0.75884052</td>
<td>0.75336505</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>IX'</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.68102740</td>
<td>1.61109497</td>
<td>-0.00016495</td>
</tr>
<tr>
<td>N</td>
<td>1.25624747</td>
<td>0.36023206</td>
<td>-0.00016839</td>
</tr>
<tr>
<td>Ge</td>
<td>0.00000878</td>
<td>-1.04180876</td>
<td>-0.00008846</td>
</tr>
<tr>
<td>N</td>
<td>-1.25624751</td>
<td>0.36020679</td>
<td>-0.00007150</td>
</tr>
<tr>
<td>C</td>
<td>-0.68106474</td>
<td>1.61107484</td>
<td>-0.00013608</td>
</tr>
<tr>
<td>C</td>
<td>2.70552766</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2.70532733</td>
<td>0.23368961</td>
<td>0.00031830</td>
</tr>
<tr>
<td>H</td>
<td>1.29984116</td>
<td>2.50140102</td>
<td>-0.00021973</td>
</tr>
<tr>
<td>H</td>
<td>-1.29989169</td>
<td>2.50137188</td>
<td>-0.00015850</td>
</tr>
<tr>
<td>H</td>
<td>2.98404762</td>
<td>-0.82322362</td>
<td>-0.00057917</td>
</tr>
<tr>
<td>H</td>
<td>3.14823116</td>
<td>0.70115377</td>
<td>-0.88806847</td>
</tr>
<tr>
<td>H</td>
<td>3.14746703</td>
<td>0.69941176</td>
<td>0.89008155</td>
</tr>
<tr>
<td>H</td>
<td>-3.14811930</td>
<td>0.70110963</td>
<td>-0.88817825</td>
</tr>
<tr>
<td>H</td>
<td>-2.98406200</td>
<td>-0.82323772</td>
<td>-0.00057224</td>
</tr>
<tr>
<td>H</td>
<td>-3.14757252</td>
<td>0.69942433</td>
<td>0.88997542</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>I'</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-0.80381010</td>
<td>1.61838581</td>
<td>-0.00010535</td>
</tr>
<tr>
<td>C</td>
<td>0.53673360</td>
<td>1.64579561</td>
<td>-0.00015341</td>
</tr>
<tr>
<td>C</td>
<td>1.24333285</td>
<td>0.31672105</td>
<td>-0.00004152</td>
</tr>
<tr>
<td>Ge</td>
<td>-0.23610794</td>
<td>-1.06506190</td>
<td>-0.00011557</td>
</tr>
<tr>
<td>N</td>
<td>-1.43092639</td>
<td>0.35870233</td>
<td>-0.00004714</td>
</tr>
<tr>
<td>C</td>
<td>-2.88478947</td>
<td>0.31609906</td>
<td>0.00004610</td>
</tr>
<tr>
<td>C</td>
<td>2.10344760</td>
<td>0.13757283</td>
<td>-1.26887990</td>
</tr>
<tr>
<td>C</td>
<td>2.10254083</td>
<td>0.13747129</td>
<td>1.26945438</td>
</tr>
<tr>
<td>H</td>
<td>-1.44243390</td>
<td>2.49936367</td>
<td>-0.0009278</td>
</tr>
<tr>
<td>H</td>
<td>1.08756214</td>
<td>2.58444311</td>
<td>-0.00023321</td>
</tr>
<tr>
<td>H</td>
<td>-3.22262137</td>
<td>-0.72280441</td>
<td>0.00016020</td>
</tr>
<tr>
<td>H</td>
<td>-3.30040230</td>
<td>0.81006375</td>
<td>0.88838380</td>
</tr>
<tr>
<td>H</td>
<td>-3.30050696</td>
<td>0.80990438</td>
<td>-0.88833225</td>
</tr>
<tr>
<td>H</td>
<td>2.57739752</td>
<td>-0.85079620</td>
<td>-1.29773738</td>
</tr>
<tr>
<td>H</td>
<td>1.50328234</td>
<td>0.24072528</td>
<td>-2.18041061</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>2.90383540</td>
<td>0.88916136</td>
<td>-1.31423948</td>
</tr>
<tr>
<td>H</td>
<td>2.57642179</td>
<td>-0.85092301</td>
<td>1.29862806</td>
</tr>
<tr>
<td>H</td>
<td>2.90293453</td>
<td>0.88901527</td>
<td>1.31541261</td>
</tr>
<tr>
<td>H</td>
<td>1.50173765</td>
<td>0.24063751</td>
<td>2.18056760</td>
</tr>
</tbody>
</table>

\[ \text{XI} \]

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-0.69800882</td>
<td>1.63386532</td>
<td>0.31890426</td>
</tr>
<tr>
<td>C</td>
<td>0.69802275</td>
<td>1.63385319</td>
<td>-0.31897117</td>
</tr>
<tr>
<td>C</td>
<td>1.41224512</td>
<td>0.30289706</td>
<td>-0.02017543</td>
</tr>
<tr>
<td>Ge</td>
<td>0.00000674</td>
<td>-1.12791531</td>
<td>-0.00000954</td>
</tr>
<tr>
<td>C</td>
<td>-1.41224700</td>
<td>0.30295752</td>
<td>0.02016918</td>
</tr>
<tr>
<td>C</td>
<td>-2.62593162</td>
<td>0.06982692</td>
<td>0.91994103</td>
</tr>
<tr>
<td>C</td>
<td>-1.80965946</td>
<td>0.20153355</td>
<td>-1.47305365</td>
</tr>
<tr>
<td>C</td>
<td>2.62598909</td>
<td>0.06981866</td>
<td>-0.91987507</td>
</tr>
<tr>
<td>C</td>
<td>1.80956603</td>
<td>0.20156065</td>
<td>1.47307930</td>
</tr>
<tr>
<td>H</td>
<td>-1.29005961</td>
<td>2.49814313</td>
<td>-0.02077998</td>
</tr>
<tr>
<td>H</td>
<td>-0.59946038</td>
<td>1.74465552</td>
<td>1.40694352</td>
</tr>
<tr>
<td>H</td>
<td>1.29007419</td>
<td>2.49814427</td>
<td>0.02066813</td>
</tr>
<tr>
<td>H</td>
<td>0.59947466</td>
<td>1.74458792</td>
<td>-1.40701627</td>
</tr>
<tr>
<td>H</td>
<td>-3.09532402</td>
<td>-0.90040683</td>
<td>0.72169637</td>
</tr>
<tr>
<td>H</td>
<td>-2.33863738</td>
<td>0.07736782</td>
<td>1.97787721</td>
</tr>
<tr>
<td>H</td>
<td>-3.39454153</td>
<td>0.84458672</td>
<td>0.78113572</td>
</tr>
<tr>
<td>H</td>
<td>-2.41058004</td>
<td>-0.69377080</td>
<td>-1.66653019</td>
</tr>
<tr>
<td>H</td>
<td>-2.39614922</td>
<td>1.07675527</td>
<td>-1.78637966</td>
</tr>
<tr>
<td>H</td>
<td>-0.94508493</td>
<td>0.15055867</td>
<td>-2.15471931</td>
</tr>
<tr>
<td>H</td>
<td>3.09534806</td>
<td>-0.90042715</td>
<td>-0.72161350</td>
</tr>
<tr>
<td>H</td>
<td>2.33876198</td>
<td>0.07737966</td>
<td>-1.97782973</td>
</tr>
<tr>
<td>H</td>
<td>3.39460828</td>
<td>0.8445937</td>
<td>-0.78101201</td>
</tr>
<tr>
<td>H</td>
<td>2.41048553</td>
<td>-0.69373065</td>
<td>1.66661218</td>
</tr>
<tr>
<td>H</td>
<td>2.39601307</td>
<td>1.07679809</td>
<td>1.78644043</td>
</tr>
<tr>
<td>H</td>
<td>0.94494514</td>
<td>0.15058226</td>
<td>2.15469254</td>
</tr>
<tr>
<td>Atom</td>
<td>X</td>
<td>Y</td>
<td>Z</td>
</tr>
<tr>
<td>------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>C</td>
<td>-2.28607731</td>
<td>0.00346427</td>
<td>0.19962120</td>
</tr>
<tr>
<td>C</td>
<td>-2.98328133</td>
<td>-1.22148539</td>
<td>0.10827528</td>
</tr>
<tr>
<td>C</td>
<td>-2.96603352</td>
<td>1.23958262</td>
<td>0.12632849</td>
</tr>
<tr>
<td>N</td>
<td>-0.85541345</td>
<td>-0.00640760</td>
<td>0.33178060</td>
</tr>
<tr>
<td>C</td>
<td>-4.35658094</td>
<td>1.22395475</td>
<td>-0.03289927</td>
</tr>
<tr>
<td>C</td>
<td>-2.21290262</td>
<td>2.56388012</td>
<td>0.17317321</td>
</tr>
<tr>
<td>C</td>
<td>-2.80317342</td>
<td>3.55232621</td>
<td>1.19313361</td>
</tr>
<tr>
<td>C</td>
<td>-2.13014195</td>
<td>3.19512977</td>
<td>-1.23114293</td>
</tr>
<tr>
<td>C</td>
<td>-5.05877948</td>
<td>0.02539167</td>
<td>-0.11805285</td>
</tr>
<tr>
<td>C</td>
<td>-4.37365140</td>
<td>-1.18393390</td>
<td>-0.05062634</td>
</tr>
<tr>
<td>C</td>
<td>-2.24978650</td>
<td>-2.55711213</td>
<td>0.13505467</td>
</tr>
<tr>
<td>C</td>
<td>-2.19140991</td>
<td>-3.17582164</td>
<td>-1.27579053</td>
</tr>
<tr>
<td>C</td>
<td>-2.84434678</td>
<td>-3.5453821</td>
<td>1.15272837</td>
</tr>
<tr>
<td>C</td>
<td>1.08288122</td>
<td>-0.00279849</td>
<td>0.32935939</td>
</tr>
<tr>
<td>C</td>
<td>1.08504393</td>
<td>-0.00374209</td>
<td>1.64076734</td>
</tr>
<tr>
<td>Si</td>
<td>2.76224173</td>
<td>-1.64935188</td>
<td>0.11986794</td>
</tr>
<tr>
<td>Si</td>
<td>2.77097272</td>
<td>1.63536056</td>
<td>0.08752416</td>
</tr>
<tr>
<td>Ge</td>
<td>0.39422639</td>
<td>-0.00428565</td>
<td>-1.07221312</td>
</tr>
<tr>
<td>C</td>
<td>3.46364194</td>
<td>1.80754428</td>
<td>-1.67107080</td>
</tr>
<tr>
<td>C</td>
<td>1.58432386</td>
<td>3.09032847</td>
<td>0.35002145</td>
</tr>
<tr>
<td>C</td>
<td>4.19814375</td>
<td>1.80789966</td>
<td>1.32527102</td>
</tr>
<tr>
<td>C</td>
<td>3.64554577</td>
<td>-1.7422783</td>
<td>-1.55614496</td>
</tr>
<tr>
<td>C</td>
<td>1.54129356</td>
<td>-3.10011879</td>
<td>0.18201470</td>
</tr>
<tr>
<td>C</td>
<td>4.01968109</td>
<td>-1.90848226</td>
<td>1.51415671</td>
</tr>
<tr>
<td>C</td>
<td>-0.26665204</td>
<td>-0.00710077</td>
<td>1.59473897</td>
</tr>
<tr>
<td>H</td>
<td>-1.19058149</td>
<td>2.34026896</td>
<td>0.48310470</td>
</tr>
<tr>
<td>H</td>
<td>-3.80984720</td>
<td>3.87994599</td>
<td>0.91218134</td>
</tr>
<tr>
<td>H</td>
<td>-2.17560301</td>
<td>4.44759793</td>
<td>1.25868898</td>
</tr>
<tr>
<td>H</td>
<td>-2.86380621</td>
<td>3.10699702</td>
<td>2.19114060</td>
</tr>
<tr>
<td>H</td>
<td>-3.12718355</td>
<td>3.41422864</td>
<td>-1.62897173</td>
</tr>
<tr>
<td>H</td>
<td>-1.63045852</td>
<td>2.52060918</td>
<td>-1.93457212</td>
</tr>
<tr>
<td>H</td>
<td>-1.56528908</td>
<td>4.13371902</td>
<td>-1.19989578</td>
</tr>
<tr>
<td>H</td>
<td>-4.89581884</td>
<td>2.16450309</td>
<td>-0.0950865</td>
</tr>
<tr>
<td>H</td>
<td>-6.13802439</td>
<td>0.03395348</td>
<td>-0.24175515</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-------</td>
<td>-------</td>
<td>--------------</td>
</tr>
</tbody>
</table>
The NPA charges of 1.

<table>
<thead>
<tr>
<th>Atom</th>
<th>No</th>
<th>Natural Charge</th>
<th>Core</th>
<th>Valence</th>
<th>Rydberg</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1</td>
<td>0.14991</td>
<td>1.99884</td>
<td>3.83234</td>
<td>0.01892</td>
<td>5.85009</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>-0.01946</td>
<td>1.99898</td>
<td>4.00393</td>
<td>0.01655</td>
<td>6.01946</td>
</tr>
<tr>
<td>C</td>
<td>3</td>
<td>-0.01584</td>
<td>1.99901</td>
<td>4.00056</td>
<td>0.01627</td>
<td>6.01584</td>
</tr>
<tr>
<td>N</td>
<td>4</td>
<td>-0.80335</td>
<td>1.99948</td>
<td>5.78784</td>
<td>0.01603</td>
<td>7.80335</td>
</tr>
<tr>
<td>C</td>
<td>5</td>
<td>-0.21607</td>
<td>1.99916</td>
<td>4.20545</td>
<td>0.01146</td>
<td>6.21607</td>
</tr>
<tr>
<td>C</td>
<td>6</td>
<td>-0.23359</td>
<td>1.99922</td>
<td>4.22307</td>
<td>0.01130</td>
<td>6.23359</td>
</tr>
<tr>
<td>C</td>
<td>7</td>
<td>-0.63561</td>
<td>1.99944</td>
<td>4.62825</td>
<td>0.00793</td>
<td>6.63561</td>
</tr>
<tr>
<td>C</td>
<td>8</td>
<td>-0.62464</td>
<td>1.99941</td>
<td>4.61753</td>
<td>0.00770</td>
<td>6.62464</td>
</tr>
<tr>
<td>C</td>
<td>9</td>
<td>-0.18825</td>
<td>1.99927</td>
<td>4.17640</td>
<td>0.01258</td>
<td>6.18825</td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td>-0.21396</td>
<td>1.99916</td>
<td>4.20331</td>
<td>0.01150</td>
<td>6.21396</td>
</tr>
<tr>
<td>C</td>
<td>11</td>
<td>-0.23009</td>
<td>1.99922</td>
<td>4.21932</td>
<td>0.01155</td>
<td>6.23009</td>
</tr>
<tr>
<td>C</td>
<td>12</td>
<td>-0.63009</td>
<td>1.99941</td>
<td>4.62292</td>
<td>0.00776</td>
<td>6.63009</td>
</tr>
<tr>
<td>C</td>
<td>13</td>
<td>-0.63224</td>
<td>1.99944</td>
<td>4.62483</td>
<td>0.00798</td>
<td>6.63224</td>
</tr>
<tr>
<td>C</td>
<td>14</td>
<td>-1.51370</td>
<td>1.99933</td>
<td>5.50057</td>
<td>0.01380</td>
<td>7.51370</td>
</tr>
<tr>
<td>C</td>
<td>15</td>
<td>-0.25800</td>
<td>1.99925</td>
<td>4.23820</td>
<td>0.02054</td>
<td>6.25800</td>
</tr>
<tr>
<td>Si</td>
<td>16</td>
<td>1.83901</td>
<td>9.99797</td>
<td>2.12702</td>
<td>0.03600</td>
<td>12.16099</td>
</tr>
<tr>
<td>Si</td>
<td>17</td>
<td>1.84585</td>
<td>9.99807</td>
<td>2.12015</td>
<td>0.03593</td>
<td>12.15415</td>
</tr>
<tr>
<td>Ge</td>
<td>18</td>
<td>0.93639</td>
<td>27.99327</td>
<td>3.05612</td>
<td>0.01422</td>
<td>31.06361</td>
</tr>
<tr>
<td>C</td>
<td>19</td>
<td>-1.14738</td>
<td>1.99942</td>
<td>5.13543</td>
<td>0.01254</td>
<td>7.14738</td>
</tr>
<tr>
<td>C</td>
<td>20</td>
<td>-1.16093</td>
<td>1.99943</td>
<td>5.14916</td>
<td>0.01235</td>
<td>7.16093</td>
</tr>
<tr>
<td>C</td>
<td>21</td>
<td>-1.16818</td>
<td>1.99943</td>
<td>5.15684</td>
<td>0.01191</td>
<td>7.16818</td>
</tr>
<tr>
<td>C</td>
<td>22</td>
<td>-1.14159</td>
<td>1.99941</td>
<td>5.12969</td>
<td>0.01249</td>
<td>7.14159</td>
</tr>
<tr>
<td>C</td>
<td>23</td>
<td>-1.16134</td>
<td>1.99942</td>
<td>5.14957</td>
<td>0.01234</td>
<td>7.16134</td>
</tr>
<tr>
<td>C</td>
<td>24</td>
<td>-1.15168</td>
<td>1.99942</td>
<td>5.13983</td>
<td>0.01244</td>
<td>7.15168</td>
</tr>
<tr>
<td>C</td>
<td>25</td>
<td>0.00919</td>
<td>1.99914</td>
<td>3.97491</td>
<td>0.01677</td>
<td>5.99081</td>
</tr>
<tr>
<td>H</td>
<td>26</td>
<td>0.23321</td>
<td>0.00000</td>
<td>0.76349</td>
<td>0.00330</td>
<td>0.76679</td>
</tr>
<tr>
<td>H</td>
<td>27</td>
<td>0.21074</td>
<td>0.00000</td>
<td>0.78759</td>
<td>0.00167</td>
<td>0.78926</td>
</tr>
<tr>
<td>H</td>
<td>28</td>
<td>0.22157</td>
<td>0.00000</td>
<td>0.77697</td>
<td>0.00146</td>
<td>0.77843</td>
</tr>
<tr>
<td>H</td>
<td>29</td>
<td>0.22075</td>
<td>0.00000</td>
<td>0.77763</td>
<td>0.00162</td>
<td>0.77925</td>
</tr>
<tr>
<td>H</td>
<td>30</td>
<td>0.21428</td>
<td>0.00000</td>
<td>0.78402</td>
<td>0.00170</td>
<td>0.78572</td>
</tr>
<tr>
<td>H</td>
<td>31</td>
<td>0.22057</td>
<td>0.00000</td>
<td>0.77792</td>
<td>0.00150</td>
<td>0.77943</td>
</tr>
<tr>
<td>H</td>
<td>32</td>
<td>0.21505</td>
<td>0.00000</td>
<td>0.78335</td>
<td>0.00160</td>
<td>0.78495</td>
</tr>
<tr>
<td>H</td>
<td>33</td>
<td>0.20517</td>
<td>0.00000</td>
<td>0.79285</td>
<td>0.00199</td>
<td>0.79483</td>
</tr>
<tr>
<td>H</td>
<td>34</td>
<td>0.20558</td>
<td>0.00000</td>
<td>0.79270</td>
<td>0.00172</td>
<td>0.79442</td>
</tr>
<tr>
<td>H</td>
<td>35</td>
<td>0.20531</td>
<td>0.00000</td>
<td>0.79271</td>
<td>0.00197</td>
<td>0.79469</td>
</tr>
<tr>
<td>H</td>
<td>36</td>
<td>0.23152</td>
<td>0.00000</td>
<td>0.76499</td>
<td>0.00349</td>
<td>0.76848</td>
</tr>
<tr>
<td>H</td>
<td>37</td>
<td>0.21989</td>
<td>0.00000</td>
<td>0.77858</td>
<td>0.00153</td>
<td>0.78011</td>
</tr>
<tr>
<td>H</td>
<td>38</td>
<td>0.21982</td>
<td>0.00000</td>
<td>0.77870</td>
<td>0.00148</td>
<td>0.78018</td>
</tr>
<tr>
<td>H</td>
<td>39</td>
<td>0.20889</td>
<td>0.00000</td>
<td>0.78945</td>
<td>0.00166</td>
<td>0.79111</td>
</tr>
<tr>
<td>H</td>
<td>40</td>
<td>0.21400</td>
<td>0.00000</td>
<td>0.78417</td>
<td>0.00182</td>
<td>0.78600</td>
</tr>
<tr>
<td>H</td>
<td>41</td>
<td>0.21626</td>
<td>0.00000</td>
<td>0.78206</td>
<td>0.00168</td>
<td>0.78374</td>
</tr>
<tr>
<td>H</td>
<td>42</td>
<td>0.22230</td>
<td>0.00000</td>
<td>0.77614</td>
<td>0.00156</td>
<td>0.77770</td>
</tr>
<tr>
<td>H</td>
<td>43</td>
<td>0.23877</td>
<td>0.00000</td>
<td>0.75997</td>
<td>0.00126</td>
<td>0.76123</td>
</tr>
<tr>
<td>H</td>
<td>44</td>
<td>0.23929</td>
<td>0.00000</td>
<td>0.75926</td>
<td>0.00145</td>
<td>0.76071</td>
</tr>
<tr>
<td>H</td>
<td>45</td>
<td>0.23324</td>
<td>0.00000</td>
<td>0.76542</td>
<td>0.00134</td>
<td>0.76676</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>46</td>
<td>0.23933</td>
<td>0.00000</td>
<td>0.75899</td>
<td>0.00168</td>
<td>0.76067</td>
</tr>
<tr>
<td>H</td>
<td>47</td>
<td>0.23685</td>
<td>0.00000</td>
<td>0.76168</td>
<td>0.00147</td>
<td>0.76315</td>
</tr>
<tr>
<td>H</td>
<td>48</td>
<td>0.23994</td>
<td>0.00000</td>
<td>0.75880</td>
<td>0.00125</td>
<td>0.76006</td>
</tr>
<tr>
<td>H</td>
<td>49</td>
<td>0.24221</td>
<td>0.00000</td>
<td>0.75644</td>
<td>0.00135</td>
<td>0.75779</td>
</tr>
<tr>
<td>H</td>
<td>50</td>
<td>0.23394</td>
<td>0.00000</td>
<td>0.76469</td>
<td>0.00137</td>
<td>0.76606</td>
</tr>
<tr>
<td>H</td>
<td>51</td>
<td>0.23849</td>
<td>0.00000</td>
<td>0.76011</td>
<td>0.00140</td>
<td>0.76151</td>
</tr>
<tr>
<td>H</td>
<td>52</td>
<td>0.23227</td>
<td>0.00000</td>
<td>0.76640</td>
<td>0.00133</td>
<td>0.76773</td>
</tr>
<tr>
<td>H</td>
<td>53</td>
<td>0.23971</td>
<td>0.00000</td>
<td>0.75886</td>
<td>0.00143</td>
<td>0.76029</td>
</tr>
<tr>
<td>H</td>
<td>54</td>
<td>0.23843</td>
<td>0.00000</td>
<td>0.76036</td>
<td>0.00121</td>
<td>0.76157</td>
</tr>
<tr>
<td>H</td>
<td>55</td>
<td>0.23906</td>
<td>0.00000</td>
<td>0.75970</td>
<td>0.00124</td>
<td>0.76094</td>
</tr>
<tr>
<td>H</td>
<td>56</td>
<td>0.23564</td>
<td>0.00000</td>
<td>0.76290</td>
<td>0.00147</td>
<td>0.76436</td>
</tr>
<tr>
<td>H</td>
<td>57</td>
<td>0.24121</td>
<td>0.00000</td>
<td>0.75708</td>
<td>0.00172</td>
<td>0.75879</td>
</tr>
<tr>
<td>H</td>
<td>58</td>
<td>0.23211</td>
<td>0.00000</td>
<td>0.76642</td>
<td>0.00147</td>
<td>0.76789</td>
</tr>
<tr>
<td>H</td>
<td>59</td>
<td>0.23899</td>
<td>0.00000</td>
<td>0.75971</td>
<td>0.00130</td>
<td>0.76101</td>
</tr>
<tr>
<td>H</td>
<td>60</td>
<td>0.23624</td>
<td>0.00000</td>
<td>0.76237</td>
<td>0.00138</td>
<td>0.76376</td>
</tr>
<tr>
<td>H</td>
<td>61</td>
<td>0.20092</td>
<td>0.00000</td>
<td>0.79769</td>
<td>0.00139</td>
<td>0.79908</td>
</tr>
<tr>
<td>H</td>
<td>62</td>
<td>0.20415</td>
<td>0.00000</td>
<td>0.79360</td>
<td>0.00225</td>
<td>0.79585</td>
</tr>
</tbody>
</table>

* Total *  
0.00000 | 91.97358 | 137.59707 | 0.42935 | 230.00000
Chapter 4

Geometry optimization, frequency calculations of compound 7 were performed at the B3LYP/6-311G(d,p) level of theory.

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.179022</td>
<td>-0.03999</td>
<td>0.206818</td>
</tr>
<tr>
<td>C</td>
<td>2.5644</td>
<td>-0.09975</td>
<td>-1.28579</td>
</tr>
<tr>
<td>C</td>
<td>4.096785</td>
<td>-0.07817</td>
<td>-1.45536</td>
</tr>
<tr>
<td>C</td>
<td>4.661339</td>
<td>1.222968</td>
<td>-0.85027</td>
</tr>
<tr>
<td>C</td>
<td>4.299008</td>
<td>1.287433</td>
<td>0.646625</td>
</tr>
<tr>
<td>C</td>
<td>2.764349</td>
<td>1.265191</td>
<td>0.803615</td>
</tr>
<tr>
<td>C</td>
<td>2.816534</td>
<td>-1.25977</td>
<td>0.920017</td>
</tr>
<tr>
<td>C</td>
<td>4.351647</td>
<td>-1.23203</td>
<td>0.763523</td>
</tr>
<tr>
<td>C</td>
<td>4.71496</td>
<td>-1.29169</td>
<td>-0.73288</td>
</tr>
<tr>
<td>C</td>
<td>4.906898</td>
<td>0.07093</td>
<td>1.376022</td>
</tr>
<tr>
<td>C</td>
<td>0.118692</td>
<td>-0.04223</td>
<td>1.590313</td>
</tr>
<tr>
<td>C</td>
<td>-1.23237</td>
<td>-0.02179</td>
<td>1.640327</td>
</tr>
<tr>
<td>C</td>
<td>-1.95124</td>
<td>-0.00927</td>
<td>0.331891</td>
</tr>
<tr>
<td>C</td>
<td>-3.60394</td>
<td>-1.80069</td>
<td>-1.67316</td>
</tr>
<tr>
<td>C</td>
<td>-4.38608</td>
<td>-1.76976</td>
<td>1.306958</td>
</tr>
<tr>
<td>C</td>
<td>-1.74581</td>
<td>-3.07488</td>
<td>0.421827</td>
</tr>
<tr>
<td>C</td>
<td>-3.62471</td>
<td>1.822614</td>
<td>-1.6116</td>
</tr>
<tr>
<td>C</td>
<td>-4.06082</td>
<td>2.05013</td>
<td>1.442878</td>
</tr>
<tr>
<td>C</td>
<td>-1.44226</td>
<td>3.036141</td>
<td>0.179477</td>
</tr>
<tr>
<td>Ge</td>
<td>-0.54477</td>
<td>-0.04121</td>
<td>-1.06956</td>
</tr>
<tr>
<td>N</td>
<td>0.711882</td>
<td>-0.05491</td>
<td>0.332665</td>
</tr>
<tr>
<td>Si</td>
<td>-2.93391</td>
<td>-1.6284</td>
<td>0.095037</td>
</tr>
<tr>
<td>Si</td>
<td>-2.78578</td>
<td>1.6929</td>
<td>0.085505</td>
</tr>
<tr>
<td>H</td>
<td>2.119814</td>
<td>0.751272</td>
<td>-1.81597</td>
</tr>
<tr>
<td>H</td>
<td>2.145318</td>
<td>-1.00818</td>
<td>-1.73636</td>
</tr>
<tr>
<td>H</td>
<td>4.336385</td>
<td>-0.1228</td>
<td>-2.52486</td>
</tr>
<tr>
<td>H</td>
<td>5.750971</td>
<td>1.257203</td>
<td>-0.97782</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>H</td>
<td>4.250056</td>
<td>2.094337</td>
<td>-1.37602</td>
</tr>
<tr>
<td>H</td>
<td>4.691864</td>
<td>2.213993</td>
<td>1.083815</td>
</tr>
<tr>
<td>H</td>
<td>2.305199</td>
<td>2.120082</td>
<td>0.292011</td>
</tr>
<tr>
<td>H</td>
<td>2.495463</td>
<td>1.34574</td>
<td>1.863835</td>
</tr>
<tr>
<td>H</td>
<td>2.395771</td>
<td>-2.17777</td>
<td>0.491463</td>
</tr>
<tr>
<td>H</td>
<td>2.553611</td>
<td>-1.25552</td>
<td>1.984358</td>
</tr>
<tr>
<td>H</td>
<td>4.780896</td>
<td>-2.09701</td>
<td>1.284486</td>
</tr>
<tr>
<td>H</td>
<td>5.805413</td>
<td>-1.29063</td>
<td>-0.85819</td>
</tr>
<tr>
<td>H</td>
<td>4.34314</td>
<td>-2.22515</td>
<td>-1.17479</td>
</tr>
<tr>
<td>H</td>
<td>6.000984</td>
<td>0.089518</td>
<td>1.290408</td>
</tr>
<tr>
<td>H</td>
<td>4.670577</td>
<td>0.115742</td>
<td>2.447276</td>
</tr>
<tr>
<td>H</td>
<td>0.749278</td>
<td>-0.04829</td>
<td>2.474546</td>
</tr>
<tr>
<td>H</td>
<td>-1.74996</td>
<td>-0.01561</td>
<td>2.596539</td>
</tr>
<tr>
<td>H</td>
<td>-4.03137</td>
<td>-2.80041</td>
<td>-1.81334</td>
</tr>
<tr>
<td>H</td>
<td>-2.81452</td>
<td>-1.66699</td>
<td>-2.42094</td>
</tr>
<tr>
<td>H</td>
<td>-4.39224</td>
<td>-1.07447</td>
<td>-1.89238</td>
</tr>
<tr>
<td>H</td>
<td>-4.83372</td>
<td>-2.76884</td>
<td>1.247584</td>
</tr>
<tr>
<td>H</td>
<td>-4.06784</td>
<td>-1.61227</td>
<td>2.342845</td>
</tr>
<tr>
<td>H</td>
<td>-5.17397</td>
<td>-1.04232</td>
<td>1.086121</td>
</tr>
<tr>
<td>H</td>
<td>-1.41943</td>
<td>-3.09289</td>
<td>1.465787</td>
</tr>
<tr>
<td>H</td>
<td>-2.22807</td>
<td>-4.0343</td>
<td>0.204098</td>
</tr>
<tr>
<td>H</td>
<td>-0.84756</td>
<td>-3.00056</td>
<td>-0.20149</td>
</tr>
<tr>
<td>H</td>
<td>-3.90342</td>
<td>2.862818</td>
<td>-1.816</td>
</tr>
<tr>
<td>H</td>
<td>-2.95152</td>
<td>1.493051</td>
<td>-2.41082</td>
</tr>
<tr>
<td>H</td>
<td>-4.53737</td>
<td>1.221937</td>
<td>-1.67506</td>
</tr>
<tr>
<td>H</td>
<td>-4.4718</td>
<td>3.05891</td>
<td>1.31926</td>
</tr>
<tr>
<td>H</td>
<td>-3.60939</td>
<td>1.998354</td>
<td>2.439205</td>
</tr>
<tr>
<td>H</td>
<td>-4.89755</td>
<td>1.344877</td>
<td>1.419531</td>
</tr>
<tr>
<td>H</td>
<td>-0.78874</td>
<td>2.877941</td>
<td>1.042692</td>
</tr>
<tr>
<td>H</td>
<td>-0.81344</td>
<td>3.047218</td>
<td>-0.71773</td>
</tr>
<tr>
<td>H</td>
<td>-1.8962</td>
<td>4.028689</td>
<td>0.278207</td>
</tr>
</tbody>
</table>
Geometry optimization, frequency calculations of compound 5d were performed at the B3LYP/6-31G(d,p) level for Ge, Si, C, N, H and M05-2X/LANL2DZ level for Au.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>4.5309</td>
<td>6.334</td>
<td>23.1526</td>
</tr>
<tr>
<td>C</td>
<td>4.4324</td>
<td>8.3496</td>
<td>22.811</td>
</tr>
<tr>
<td>Ge</td>
<td>4.5563</td>
<td>3.9886</td>
<td>23.441</td>
</tr>
<tr>
<td>N</td>
<td>3.8707</td>
<td>3.0532</td>
<td>24.8275</td>
</tr>
<tr>
<td>C</td>
<td>3.5085</td>
<td>3.5893</td>
<td>26.1191</td>
</tr>
<tr>
<td>C</td>
<td>2.1668</td>
<td>3.7344</td>
<td>26.4828</td>
</tr>
<tr>
<td>C</td>
<td>4.5569</td>
<td>4.0569</td>
<td>26.9375</td>
</tr>
<tr>
<td>C</td>
<td>4.1959</td>
<td>4.7219</td>
<td>28.1123</td>
</tr>
<tr>
<td>C</td>
<td>6.0058</td>
<td>3.8654</td>
<td>26.5883</td>
</tr>
<tr>
<td>C</td>
<td>6.7413</td>
<td>3.0673</td>
<td>27.654</td>
</tr>
<tr>
<td>C</td>
<td>6.7227</td>
<td>5.1875</td>
<td>26.3155</td>
</tr>
<tr>
<td>H</td>
<td>6.038</td>
<td>3.3293</td>
<td>25.7445</td>
</tr>
<tr>
<td>H</td>
<td>6.4788</td>
<td>3.3878</td>
<td>28.5415</td>
</tr>
<tr>
<td>H</td>
<td>7.7089</td>
<td>3.1822</td>
<td>27.5376</td>
</tr>
<tr>
<td>H</td>
<td>6.5134</td>
<td>2.1181</td>
<td>27.5704</td>
</tr>
<tr>
<td>H</td>
<td>6.4155</td>
<td>5.8667</td>
<td>26.952</td>
</tr>
<tr>
<td>H</td>
<td>6.5323</td>
<td>5.4817</td>
<td>25.4026</td>
</tr>
<tr>
<td>H</td>
<td>7.6924</td>
<td>5.0605</td>
<td>26.421</td>
</tr>
<tr>
<td>C</td>
<td>2.8876</td>
<td>4.9053</td>
<td>28.4579</td>
</tr>
<tr>
<td>H</td>
<td>4.8773</td>
<td>5.0545</td>
<td>28.6834</td>
</tr>
<tr>
<td>C</td>
<td>1.8829</td>
<td>4.4035</td>
<td>27.6795</td>
</tr>
<tr>
<td>H</td>
<td>2.6724</td>
<td>5.387</td>
<td>29.2471</td>
</tr>
<tr>
<td>H</td>
<td>0.9803</td>
<td>4.5123</td>
<td>27.9523</td>
</tr>
<tr>
<td>Element</td>
<td>x</td>
<td>y</td>
<td>z</td>
</tr>
<tr>
<td>---------</td>
<td>----</td>
<td>----</td>
<td>-----</td>
</tr>
<tr>
<td>C</td>
<td>1.0213</td>
<td>3.1963</td>
<td>25.6099</td>
</tr>
<tr>
<td>C</td>
<td>0.0421</td>
<td>2.3559</td>
<td>26.4355</td>
</tr>
<tr>
<td>C</td>
<td>0.251</td>
<td>4.333</td>
<td>24.9115</td>
</tr>
<tr>
<td>H</td>
<td>1.4172</td>
<td>2.6079</td>
<td>24.9043</td>
</tr>
<tr>
<td>H</td>
<td>-0.4527</td>
<td>2.9384</td>
<td>27.0466</td>
</tr>
<tr>
<td>H</td>
<td>0.5448</td>
<td>1.6889</td>
<td>26.9557</td>
</tr>
<tr>
<td>H</td>
<td>-0.5821</td>
<td>1.8985</td>
<td>25.8354</td>
</tr>
<tr>
<td>H</td>
<td>0.8772</td>
<td>4.857</td>
<td>24.3623</td>
</tr>
<tr>
<td>H</td>
<td>-0.1564</td>
<td>4.9134</td>
<td>25.5844</td>
</tr>
<tr>
<td>H</td>
<td>-0.4423</td>
<td>3.9521</td>
<td>24.3369</td>
</tr>
<tr>
<td>C</td>
<td>3.9249</td>
<td>1.6808</td>
<td>24.5689</td>
</tr>
<tr>
<td>C</td>
<td>4.404</td>
<td>1.316</td>
<td>23.3937</td>
</tr>
<tr>
<td>H</td>
<td>3.6317</td>
<td>1.0399</td>
<td>25.2062</td>
</tr>
<tr>
<td>C</td>
<td>4.9159</td>
<td>2.366</td>
<td>22.4706</td>
</tr>
<tr>
<td>H</td>
<td>4.4216</td>
<td>0.399</td>
<td>23.1402</td>
</tr>
<tr>
<td>Si</td>
<td>6.8309</td>
<td>2.0577</td>
<td>22.34</td>
</tr>
<tr>
<td>Si</td>
<td>3.7755</td>
<td>2.5413</td>
<td>20.8887</td>
</tr>
<tr>
<td>C</td>
<td>7.5486</td>
<td>1.5397</td>
<td>23.984</td>
</tr>
<tr>
<td>H</td>
<td>7.1182</td>
<td>0.7134</td>
<td>24.2823</td>
</tr>
<tr>
<td>H</td>
<td>7.3915</td>
<td>2.2471</td>
<td>24.646</td>
</tr>
<tr>
<td>H</td>
<td>8.5118</td>
<td>1.3906</td>
<td>23.8858</td>
</tr>
<tr>
<td>C</td>
<td>7.1616</td>
<td>0.653</td>
<td>21.1761</td>
</tr>
<tr>
<td>H</td>
<td>6.7992</td>
<td>-0.1753</td>
<td>21.5507</td>
</tr>
<tr>
<td>H</td>
<td>8.1316</td>
<td>0.5562</td>
<td>21.0488</td>
</tr>
<tr>
<td>H</td>
<td>6.7388</td>
<td>0.8364</td>
<td>20.3104</td>
</tr>
<tr>
<td>C</td>
<td>7.6999</td>
<td>3.6337</td>
<td>21.8926</td>
</tr>
<tr>
<td>H</td>
<td>7.6033</td>
<td>4.2786</td>
<td>22.6237</td>
</tr>
<tr>
<td>H</td>
<td>7.3044</td>
<td>4.0045</td>
<td>21.0779</td>
</tr>
<tr>
<td>H</td>
<td>8.6507</td>
<td>3.4523</td>
<td>21.7435</td>
</tr>
<tr>
<td>C</td>
<td>2.004</td>
<td>2.5232</td>
<td>21.4889</td>
</tr>
<tr>
<td>H</td>
<td>1.8633</td>
<td>3.2608</td>
<td>22.1181</td>
</tr>
<tr>
<td>H</td>
<td>1.8179</td>
<td>1.6707</td>
<td>21.9363</td>
</tr>
<tr>
<td>H</td>
<td>1.3975</td>
<td>2.628</td>
<td>20.7251</td>
</tr>
<tr>
<td>C</td>
<td>3.9877</td>
<td>1.1105</td>
<td>19.6703</td>
</tr>
<tr>
<td>H</td>
<td>3.6881</td>
<td>0.2761</td>
<td>20.0885</td>
</tr>
<tr>
<td>H</td>
<td>4.9394</td>
<td>1.0258</td>
<td>19.4302</td>
</tr>
<tr>
<td>H</td>
<td>3.4643</td>
<td>1.2838</td>
<td>18.8628</td>
</tr>
<tr>
<td>C</td>
<td>4.0392</td>
<td>4.1153</td>
<td>19.8812</td>
</tr>
<tr>
<td>H</td>
<td>3.5279</td>
<td>4.0629</td>
<td>19.0483</td>
</tr>
<tr>
<td>H</td>
<td>4.996</td>
<td>4.21</td>
<td>19.6703</td>
</tr>
<tr>
<td>H</td>
<td>3.7472</td>
<td>4.8912</td>
<td>20.4013</td>
</tr>
<tr>
<td>N</td>
<td>4.5198</td>
<td>9.325</td>
<td>23.7218</td>
</tr>
<tr>
<td>N</td>
<td>4.2372</td>
<td>8.9683</td>
<td>21.6318</td>
</tr>
<tr>
<td>C</td>
<td>4.2075</td>
<td>10.3407</td>
<td>21.8079</td>
</tr>
<tr>
<td>C</td>
<td>4.3822</td>
<td>10.5705</td>
<td>23.1093</td>
</tr>
<tr>
<td>H</td>
<td>4.0866</td>
<td>10.9937</td>
<td>21.1288</td>
</tr>
<tr>
<td>H</td>
<td>4.4079</td>
<td>11.4169</td>
<td>23.5367</td>
</tr>
<tr>
<td>C</td>
<td>4.7696</td>
<td>9.067</td>
<td>25.1334</td>
</tr>
<tr>
<td>---</td>
<td>--------</td>
<td>-------</td>
<td>---------</td>
</tr>
<tr>
<td>C</td>
<td>6.1079</td>
<td>9.0489</td>
<td>25.5262</td>
</tr>
<tr>
<td>C</td>
<td>3.686</td>
<td>8.8655</td>
<td>25.9882</td>
</tr>
<tr>
<td>C</td>
<td>6.3626</td>
<td>8.8111</td>
<td>26.8757</td>
</tr>
<tr>
<td>C</td>
<td>7.2772</td>
<td>9.2</td>
<td>24.5915</td>
</tr>
<tr>
<td>C</td>
<td>8.1958</td>
<td>10.3185</td>
<td>25.0716</td>
</tr>
<tr>
<td>C</td>
<td>8.041</td>
<td>7.878</td>
<td>24.4605</td>
</tr>
<tr>
<td>H</td>
<td>6.9288</td>
<td>9.4499</td>
<td>23.6894</td>
</tr>
<tr>
<td>H</td>
<td>7.6666</td>
<td>11.1186</td>
<td>25.2607</td>
</tr>
<tr>
<td>H</td>
<td>8.8548</td>
<td>10.5221</td>
<td>24.3732</td>
</tr>
<tr>
<td>H</td>
<td>8.6633</td>
<td>10.0324</td>
<td>25.8827</td>
</tr>
<tr>
<td>H</td>
<td>8.3111</td>
<td>7.5676</td>
<td>25.348</td>
</tr>
<tr>
<td>H</td>
<td>8.8359</td>
<td>8.013</td>
<td>23.904</td>
</tr>
<tr>
<td>H</td>
<td>7.4611</td>
<td>7.2069</td>
<td>24.0422</td>
</tr>
<tr>
<td>C</td>
<td>5.3335</td>
<td>8.5692</td>
<td>27.7522</td>
</tr>
<tr>
<td>H</td>
<td>7.2614</td>
<td>8.8151</td>
<td>27.1921</td>
</tr>
<tr>
<td>C</td>
<td>4.0171</td>
<td>8.5974</td>
<td>27.3194</td>
</tr>
<tr>
<td>H</td>
<td>5.5272</td>
<td>8.3818</td>
<td>28.6615</td>
</tr>
<tr>
<td>H</td>
<td>3.3278</td>
<td>8.4282</td>
<td>27.945</td>
</tr>
<tr>
<td>C</td>
<td>2.2642</td>
<td>8.7163</td>
<td>25.4644</td>
</tr>
<tr>
<td>C</td>
<td>1.6493</td>
<td>7.3459</td>
<td>25.7372</td>
</tr>
<tr>
<td>C</td>
<td>1.3472</td>
<td>9.8691</td>
<td>25.879</td>
</tr>
<tr>
<td>H</td>
<td>2.3398</td>
<td>8.7808</td>
<td>24.4714</td>
</tr>
<tr>
<td>H</td>
<td>2.2771</td>
<td>6.6446</td>
<td>25.4571</td>
</tr>
<tr>
<td>H</td>
<td>0.8147</td>
<td>7.2552</td>
<td>25.2316</td>
</tr>
<tr>
<td>H</td>
<td>1.4667</td>
<td>7.2532</td>
<td>26.6938</td>
</tr>
<tr>
<td>H</td>
<td>1.7599</td>
<td>10.7236</td>
<td>25.6317</td>
</tr>
<tr>
<td>H</td>
<td>1.2031</td>
<td>9.8429</td>
<td>26.8466</td>
</tr>
<tr>
<td>H</td>
<td>0.4831</td>
<td>9.7804</td>
<td>25.4208</td>
</tr>
<tr>
<td>C</td>
<td>4.0581</td>
<td>8.1863</td>
<td>20.3468</td>
</tr>
<tr>
<td>C</td>
<td>2.7643</td>
<td>7.7832</td>
<td>20.0049</td>
</tr>
<tr>
<td>C</td>
<td>5.1895</td>
<td>7.9324</td>
<td>19.543</td>
</tr>
<tr>
<td>C</td>
<td>2.6398</td>
<td>7.0416</td>
<td>18.841</td>
</tr>
<tr>
<td>C</td>
<td>1.5549</td>
<td>8.0674</td>
<td>20.8742</td>
</tr>
<tr>
<td>C</td>
<td>1.0268</td>
<td>6.7715</td>
<td>21.4852</td>
</tr>
<tr>
<td>C</td>
<td>0.4504</td>
<td>8.7808</td>
<td>20.0922</td>
</tr>
<tr>
<td>H</td>
<td>1.8437</td>
<td>8.668</td>
<td>21.6198</td>
</tr>
<tr>
<td>H</td>
<td>0.7581</td>
<td>6.1569</td>
<td>20.7723</td>
</tr>
<tr>
<td>H</td>
<td>0.2468</td>
<td>6.9711</td>
<td>22.049</td>
</tr>
<tr>
<td>H</td>
<td>1.7246</td>
<td>6.3564</td>
<td>22.0308</td>
</tr>
<tr>
<td>H</td>
<td>0.0944</td>
<td>8.1803</td>
<td>19.4047</td>
</tr>
<tr>
<td>H</td>
<td>0.8145</td>
<td>9.585</td>
<td>19.6666</td>
</tr>
<tr>
<td>H</td>
<td>-0.2732</td>
<td>9.0348</td>
<td>20.7069</td>
</tr>
<tr>
<td>C</td>
<td>3.7283</td>
<td>6.7635</td>
<td>18.0371</td>
</tr>
<tr>
<td>H</td>
<td>1.7833</td>
<td>6.7151</td>
<td>18.59</td>
</tr>
<tr>
<td>C</td>
<td>4.9757</td>
<td>7.2008</td>
<td>18.3972</td>
</tr>
<tr>
<td>H</td>
<td>3.6119</td>
<td>6.2677</td>
<td>17.2369</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>H</td>
<td>5.7148</td>
<td>6.9952</td>
<td>17.8371</td>
</tr>
<tr>
<td>C</td>
<td>6.5815</td>
<td>8.3758</td>
<td>19.9394</td>
</tr>
<tr>
<td>C</td>
<td>7.3731</td>
<td>7.1706</td>
<td>20.4523</td>
</tr>
<tr>
<td>C</td>
<td>7.3461</td>
<td>9.0186</td>
<td>18.7719</td>
</tr>
<tr>
<td>H</td>
<td>6.5042</td>
<td>9.0469</td>
<td>20.6778</td>
</tr>
<tr>
<td>H</td>
<td>7.5815</td>
<td>8.3294</td>
<td>18.1172</td>
</tr>
<tr>
<td>H</td>
<td>8.1631</td>
<td>9.4419</td>
<td>19.1172</td>
</tr>
<tr>
<td>H</td>
<td>6.7813</td>
<td>9.6958</td>
<td>18.3463</td>
</tr>
<tr>
<td>H</td>
<td>6.9333</td>
<td>6.8018</td>
<td>21.2452</td>
</tr>
<tr>
<td>H</td>
<td>8.2834</td>
<td>7.4547</td>
<td>20.6887</td>
</tr>
<tr>
<td>H</td>
<td>7.4167</td>
<td>6.4854</td>
<td>19.7539</td>
</tr>
</tbody>
</table>

**Supplementary reference**