

THE CHEMISTRY OF CARBENE-STABILIZED
MAIN GROUP DIATOMIC ALLOTROPES

by

MARIHAM ABRAHAM

(Under the Direction of Gregory H. Robinson)

ABSTRACT

The syntheses and molecular structures of carbene-stabilized arsenic derivatives of AsCl_3 ($\text{L}^1:\text{AsCl}_3$ (**1**); $\text{L}^1 = :\text{C}\{\text{N}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{CH}\}_2$), and As_2 ($\text{L}^1:\text{As}-\text{As}:\text{L}^1$ (**2**)), are presented herein. The potassium graphite reduction of **1** afforded the carbene-stabilized diarsenic complex, **2**. Notably, compound **2** is the first Lewis base stabilized diatomic molecule of the Group 13–15 elements, in the formal oxidation state of zero, in the fourth period or lower of the Periodic Table. Compound **2** contains one As–As σ -bond and two lone pairs of electrons on each arsenic atom. In an effort to study the chemistry of the electron-rich compound **2**, it was combined with an electron-deficient Lewis acid, GaCl_3 . The addition of two equivalents of GaCl_3 to **2** resulted in one-electron oxidation of **2** to give $[\text{L}^1:\text{As}=\text{As}:\text{L}^1]^{+}[\text{GaCl}_4]^{-}$ (**6⁺[GaCl₄]⁻**). Conversely, the addition of four equivalents of GaCl_3 to **2** resulted in two- electron oxidation of **2** to give $[\text{L}^1:\text{As}=\text{As}:\text{L}^1]^{2+}[\text{GaCl}_4]^{-}_2$ (**6²⁺[GaCl₄]⁻₂**). Strikingly, **6⁺** represents the first arsenic radical to be structurally characterized in the solid state. The research project also explored the reactivity of carbene-stabilized disilicon, ($\text{L}^1:\text{Si}=\text{Si}:\text{L}^1$ (**7**)), with borane. The reaction of **7** with $\text{BH}_3\cdot\text{THF}$ afforded two unique compounds: one containing a parent

silylene ($:SiH_2$) unit (**8**), and another containing a three-membered silylene ring (**9**). Notably, **8** is the first example of a “push–pull” stabilized parent silylene, while **9** is the first example of a three-membered cyclic silylene, both of which are persistent under ambient conditions.

INDEX WORDS: arsenic, N-heterocyclic carbene, diatomic, gallium, metal–metal bonds, main-group, oxidation, oxidation-state, “push-pull”, radical, reduction, silicon, silylene, sterically demanding ligands

THE CHEMISTRY OF CARBENE-STABILIZED
MAIN GROUP DIATOMIC ALLOTROPES

by

MARIHAM ABRAHAM

B.S., Louisiana State University, 2008

A Dissertation Submitted to the Graduate Faculty of The University of Georgia in Partial
Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

ATHENS, GEORGIA

2013

©2013

Mariham Abraham

All Rights Reserved

THE CHEMISTRY OF CARBENE-STABILIZED
MAIN GROUP DIATOMIC ALLOTROPES

by

MARIHAM ABRAHAM

Major Professor: Gregory H. Robinson

Committee: George F. Majetich
Robert S. Phillips

Electronic version approved:

Maureen Grasso
Dean of the Graduate School
The University of Georgia
August 2013

DEDICATION

I dedicate my dissertation to my parents, Feleklek Mengistu and Yohannes Abraham, for their endless love, support and sacrifices they had to make to provide for my education. Their continued words of encouragement and faith in me have given me the strength to achieve this goal. My dedication extends to my brothers, Abraham Yohannes and Daniel Yohannes, and my sister, Hemen Yohannes, who have also been extremely supportive and my grandmother, Gorfenesh Abayere, whose love, encouragement, and prayers have always been my valuable assets.

I also dedicate my dissertation to my uncle, Dr. Ashagre Yigletu, his wife, Menbere Netere, and their children, Agereneshe Ashagre and Yonas Ashagre, who provided me a loving home when I moved to the United States. They have been a constant source of support, advice, and motivation and have instilled in me the importance of hard work and higher education. I am forever thankful for their kindness and words of wisdom that have enabled me to achieve my goals.

This dissertation is also lovingly dedicated in memory of my great grandparents, Azmara Akalu and Shambele Zeleke Gelaye, my grandparents, Amsale Yigletu and Abraham Hailu, and my uncle, Solomon Abraham. Despite being unable to see the completion of my degree, I have no doubt they are smiling down on me. I am forever grateful to Emaye Azmara and Emaye Amsale whose prayers, and support have strengthened me. I praise God for giving me such a wonderful family, and I thank them for all the love and care they have given me throughout my life.

ACKNOWLEDGEMENTS

First and foremost, I would like to thank God for directing my life. I thank him for all the people he has led me to meet that helped me in numerous ways. I have come this far in life due to his many blessings.

I would like to sincerely thank my advisor, Dr. Gregory H. Robinson, for giving me the opportunity to be a part of his research team. His support, guidance, and encouragement during my moments of frustration have enabled me to accomplish my goal. I would also like to thank my committee members, Dr. George F. Majetich and Dr. Robert S. Philips, for their helpful advice and inputs. I am very grateful to Dr. Yuzhong Wang for his guidance in getting my graduate career started on the right foot, and for his much valued insight and motivation throughout my studies. I would also like to thank Dr. Pingrong Wei for his expertise in helping me obtain my X-ray crystallographic data. I would also like to thank my colleague, Robert Gilliard, for the enlightening discussions and helping me tirelessly with my writings. Our friendship has made my life in graduate school easier and memorable. I am very thankful for my friend, Dr. Magdelena Angelova, who constantly motivated me throughout my years at Louisiana State University and beyond. I would also like to thank Koustubh Dube, Vivian Ezeh, and Matthew Mendecino who eased my transition into graduate school with their friendship. A special thanks to Daniel Sexton, Jared Smith, Robert Heider, and Avery Wines for working with me on various projects.

I would like to thank my cousin, Hanna Yigletu, whose guidance ever since I moved to the United States was invaluable. I feel very fortunate to have her nearby not only in Louisiana but also in Georgia as I transitioned through various stages in my life. I thank her and her family for their love and support at all times. I would also like to thank my cousin, Saba McMillian, and her family who were also very supportive and Dr. Yaw Twum-Antwi for his care and encouragement throughout the years. I am very grateful to my aunt, Dr. Yeshihareg Abraham, and her family whose support, motivation, and prayers have always been uplifting. I would also like to thank my aunt, Sara Abraham, and her family who took time to visit me when I started my journey at The University of Georgia, and their valuable advice. I am also thankful to my aunts, Elizabeth Abraham and Nigist Fikru, and their families who always encouraged me throughout my studies. A special thanks to my cousins, Tizita Elias and Hanna Hailu, who shaped my attitude and view of life, and were great role models. I would also like to thank all the wonderful family in the Ethiopian Community Association of Baton Rouge for the memorable times I spent there.

I am very thankful for Almaz Getachew, Getachew Ersido, Lemlem Getachew, Bealemlay Arega, Yibeltal Arega, and my God daughter, Sena Telila, for being a loving and supportive family. The outpouring love and kindness I received from Almaz and Yibeltal have always made me feel at home. Finally, I would like to thank a very special person in my life, Ashenafi Arega, for motivating me and being there for me and in all possible ways. His unwavering patience and advice have always put things back in perspective for me when I felt overwhelmed. I could not imagine going through this journey without him and I feel truly blessed to have him in my life.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS.....	v
LIST OF TABLES.....	ix
LIST OF FIGURES.....	xi
LIST OF SCHEMES.....	xiii
CHAPTER	
1 INTRODUCTION.....	1
1.1 Purpose of Study.....	1
1.2 Organometallic Chemistry.....	2
1.3 Synthetic Techniques of Organometallic Compounds.....	5
1.4 Low-Valent Main Group Element-Element Bonds.....	6
1.5 Stable Carbenes.....	12
1.6 Carbene-Stabilized Highly Reactive Molecules.....	20
1.7 Conclusion.....	38
2 RESULTS AND DISCUSSIONS.....	39
2.1 Carbene-Stabilized Diarsenic.....	40
2.2 Oxidation of Carbene-Stabilized Diarsenic.....	49
2.3 Cleavage of Carbene-Stabilized Disilicon.....	59

3 CONCLUSION.....	68
3.1 Concluding Remarks.....	68
4 EXPERIMENTAL.....	71
4.1 General Background.....	71
4.2 Preparation of Starting Materials.....	73
4.3 Syntheses of Carbene-Stabilized Diarsenic.....	74
4.4 Syntheses of Oxidized Diarsenic Derivatives.....	75
4.5 Syntheses of “Push–Pull” Stabilized Silylenes.....	77
REFERENCES.....	79
APPENDICES	
A CRYSTALLOGRAPHIC DATA.....	94
B RESEARCH PUBLICATIONS.....	138

LIST OF TABLES

Table 1: Selected bond lengths [Å] and angles [°] of 1	44
Table 2: Selected bond lengths [Å] and angles [°] of 2	46
Table 3: Selected bond lengths [Å] and angles [°] of 6⁺	52
Table 4: Selected bond lengths [Å] and angles [°] of 6²⁺	56
Table 5: Selected bond lengths [Å] and angles [°] of 8	63
Table 6: Selected bond lengths [Å] and angles [°] of 9	66
Table 7: Crystal data and structure refinement of 1	94
Table 8: Atomic coordinates (x 10 ⁴) and equivalent isotropic displacement parameters (Å x 10 ³) of 1	95
Table 9: Bond lengths [Å] of 1	96
Table 10: Bond angles [°] of 1	97
Table 11: Crystal data and structure refinement of 2	98
Table 12: Atomic coordinates (x 10 ⁴) and equivalent isotropic displacement parameters (Å x 10 ³) of 2	99
Table 13: Bond lengths [Å] of 2	100
Table 14: Bond angles [°] of 2	101
Table 15: Crystal data and structure refinement of 6⁺[GaCl₄]⁻	102
Table 16: Atomic coordinates (x 10 ⁴) and equivalent isotropic displacement parameters (Å x 10 ³) of 6⁺[GaCl₄]⁻	103
Table 17: Bond lengths [Å] of 6⁺[GaCl₄]⁻	105

Table 18: Bond angles [°] of $\mathbf{6}^{+}[\text{GaCl}_4]^-$	107
Table 19: Crystal data and structure refinement of $\mathbf{6}^{2+}[\text{GaCl}_4^-]_2$	110
Table 20: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA} \times 10^3$) of $\mathbf{6}^{2+}[\text{GaCl}_4^-]_2$	111
Table 21: Bond lengths [\AA] of $\mathbf{6}^{2+}[\text{GaCl}_4^-]_2$	112
Table 22: Bond angles [°] of $\mathbf{6}^{2+}[\text{GaCl}_4^-]_2$	113
Table 23: Crystal data and structure refinement of $\mathbf{8}$	114
Table 24: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA} \times 10^3$) of $\mathbf{8}$	115
Table 25: Bond lengths [\AA] of $\mathbf{8}$	117
Table 26: Bond angles [°] of $\mathbf{8}$	123
Table 27: Crystal data and structure refinement of $\mathbf{9}$	129
Table 28: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA} \times 10^3$) of $\mathbf{9}$	130
Table 29: Bond lengths [\AA] of $\mathbf{9}$	132
Table 30: Bond angles [°] of $\mathbf{9}$	134

LIST OF FIGURES

Figure 1: Zeise's salt.....	3
Figure 2: Structure of ferrocene, $(C_5H_5)_2Fe$	4
Figure 3: Triplet vs singlet interactions of element-element bonds.....	8
Figure 4: π - σ^* orbital mixing.....	9
Figure 5: Unslipped vs slipped triple bond.....	11
Figure 6: Triple bond model for heavier main group metallynes.....	11
Figure 7: Examples of two early carbenes.....	13
Figure 8: Electronic configuration of carbenes.....	14
Figure 9: Inductive and mesomeric effects in carbenes.....	15
Figure 10: Common NHC ligands.....	20
Figure 11: Polymorphic Structures of diborene.....	23
Figure 12: Conceptual progression from disilene to disilyne to carbene-stabilized disilicon of low-valent silicon-silicon compounds.....	29
Figure 13: Canonical forms of carbene-stabilized P_2	36
Figure 14: The Structure of P_4 , white phosphorus.....	36
Figure 15: Various bonding modes for Diphosphorus and Diasrenic ($E = P$ or As).....	40
Figure 16: Examples of L: occupying equatorial (a) and axial positions (b) in $L:AsCl_3$ complexes.....	43
Figure 17: Molecular structure of 1	44
Figure 18: Molecular structure of 2	46

Figure 19: Optimized geometry of 2-H model in C ₂ symmetry.....	47
Figure 20: LMOs of 2-H with C _i symmetry.....	48
Figure 21: Molecular structure of 6^{•+}	52
Figure 22: LMOs of 6-H^{•+} with C ₂ symmetry.....	53
Figure 23: Room-temperature X-band EPR spectrum of 6^{•+}	54
Figure 24: Molecular structure of 6²⁺	56
Figure 25: LMOs of 6-H²⁺ with C _i symmetry.....	57
Figure 26: Molecular orbital diagrams of 2 , 6^{•+} , and 6²⁺	58
Figure 27: Molecular structure of 8	63
Figure 28: Molecular structure of 9	66

LIST OF SCHEMES

Scheme 1: Preparation of ferrocene, $(C_5H_5)_2Fe$	4
Scheme 2: Synthesis of distannene, $R_2Sn=SnR_2$ ($R = -CH(Me_3Si)_2$).....	7
Scheme 3: Synthesis of digallyne, $Na_2[RGa \equiv GaR]$ ($R = 2,6-(2,4,6-iPr_3C_6H_2)_2C_6H_3-$)...	10
Scheme 4: Synthesis of NHC-chromium complex.....	16
Scheme 5: Synthesis of NHC-mercury complex.....	16
Scheme 6: NHC dimerization.....	17
Scheme 7: Synthesis of the first crystalline NHC.....	18
Scheme 8: Synthesis of alkyl substituted NHC.....	18
Scheme 9: First synthetic route for preparation of CAAC.....	19
Scheme 10: Alternate synthetic route for preparation of CAAC.....	20
Scheme 11: Synthesis of NHC-stabilized diborene 19 and diborane 20	22
Scheme 12: Synthesis of NHC-stabilized diborene 23 and diboryne 24	24
Scheme 13: Synthesis of CAAC-stabilized parent borylene 27	26
Scheme 14: Oxidation and protonation CAAC-stabilized parent borylene 27	27
Scheme 15: Synthesis of NHC-stabilized digallane 31 and Ga_6 octahedron 32	28
Scheme 16: Synthesis of NHC-stabilized bis-silylene 34 and disilicon 35	30
Scheme 17: Syntheses of NHC-stabilized dihalosilylenes 39 and 41	33
Scheme 18: Synthesis of NHC-stabilized L:P-P:L 43 and 44	35
Scheme 19: Synthesis of CAAC-stabilized L':P-P:L' 45	35
Scheme 20: Proposed reaction pathway for the formation of NHC-stabilized P_{12} 52	37

Scheme 21: Synthesis of 1	41
Scheme 22: Synthesis of 2	42
Scheme 23: Synthesis of 6^{•+}[GaCl₄]⁻ and 6²⁺[GaCl₄⁻]₂	50
Scheme 24: Synthesis of 8	60
Scheme 25: Synthesis of 9	64

CHAPTER 1

INTRODUCTION

1.1 Purpose of Study

Over the last four decades there has been considerable interest in the synthesis and characterization of molecules that feature homonuclear bonds between the heavier ($n \geq 3$) main group elements. This is due, in part, to the unusual structures and properties exhibited by these compounds. Such discoveries afford new insights which facilitate the development of new bonding models¹ thus enhancing our understanding of the fundamental principles of structure and bonding. Consequently, we continue to explore different synthetic methods that may afford unique bonding modes among the heavier main group elements. In particular, isolation of molecules in low oxidation states will be pursued using a class of organic bases known as N-heterocyclic carbenes (NHCs).

Another aspect of this research project focuses on reactivity studies of these NHC-stabilized molecules with various reagents. Their increased solubility compared to their known allotropes facilitates further chemical transformations. Our research will mimic reactions, such as hydroboration of alkenes,² to gain further insight on how the heavier main group elements would react in this regard. Reactivity studies are essential in studying the characteristics of newly synthesized compounds, which could eventually be probed to target their utility in various industrial processes.³

1.2 Organometallic Chemistry

Organometallic chemistry is an interdisciplinary field that combines both traditional-organic chemistry and inorganic chemistry. In the simplest form, it may be defined as the chemistry of compounds containing at least one carbon-metal bond. However, the term “metal” could cause some ambiguity since it does not clearly indicate whether metalloids, which have some metallic character, fall into this category. Consequently, some chemists prefer to narrow this definition in electronic terms; that is, compounds containing carbon σ-bound to a more electropositive element.^{4,5} The ever-increasing utility of organometallic compounds in manufacturing⁶ and pharmaceutical⁷ industries has made them an important area of research.

The first organometallic compound was synthesized in 1760 by the French chemist Cadet de Gassicourt. In an attempt to make invisible ink, Cadet synthesized a red fuming liquid from the reaction of potassium acetate with arsenic trioxide.⁸ The liquid was later characterized by Bunsen as cacodyl oxide $(\text{AsMe}_2)_2\text{O}$.⁹ In 1827, W.C. Zeise synthesized yellow needle-like crystals (now known as “Zeise’s salt”) upon refluxing a mixture of PtCl_4 and PtCl_2 in ethanol, followed by addition of KCl solution.¹⁰ Zeise’s proposal suggesting that the compound contained an ethylene group was subject to controversy.¹¹ While the percent composition was verified by Birnbaum⁹ in 1868, its formulation, $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]\cdot\text{H}_2\text{O}$, and structure was definitively determined only in 1954 via X-ray crystallography.¹² Indeed, the anion revealed an ethylene group bound perpendicular to the PtCl_3 plane using the π-electrons of ethylene (Figure 1). Zeise’s salt is the first isolated compound containing an unsaturated organic molecule bonded to a metal.

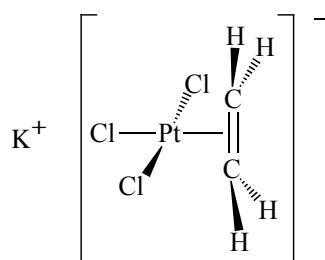
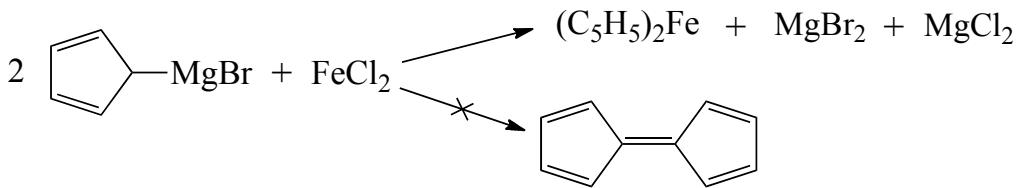


Figure 1. Zeise's salt.

The synthesis and isolation of the first metal alkyl, diethylzinc ($[C_2H_5]_2Zn$), by Edward Frankland in 1849 sparked a growing interest in the field of organometallic chemistry.¹³ The various organozinc derivatives that followed were subsequently used to synthesize many main group metal alkyls. However, they were not ideal candidates due to the tedious manipulation required to overcome their pyrophoric nature. The discovery of alkylmagnesium halides by Victor Grignard in 1900¹⁴ quickly replaced organozinc compounds. The ease in preparative and handling processes of these reagents, now known as Grignard reagents, have made them convenient and versatile tools in studying various organic reactions.¹⁵ Grignard was awarded the 1912 Nobel Prize in Chemistry in recognition of his discovery and substantial contribution to understanding the chemistry of these reagents.

A revolutionary discovery at the end of 1951 marked a new era toward rapid development in the field of modern organometallic chemistry. In an attempt to synthesize fulvalene ($C_{10}H_8$), Pauson and Kealy treated the Grignard reagent *cyclo-C₅H₅MgBr* with anhydrous iron(III) chloride after initial reduction of $FeCl_3$ to $FeCl_2$ by Grignard reagent (Scheme 1).¹⁶ The analytical data of the yellow crystals obtained proved to be $FeC_{10}H_{10}$. Concurrently, Miller and co-workers also synthesized the identical compound from the reaction of reduced iron and cyclopentadiene vapor in the presence of metal oxides.¹⁷



Scheme 1. Preparation of ferrocene, $(\text{C}_5\text{H}_5)_2\text{Fe}$.

Both research groups proposed a compound with 10 valence electrons, wherein the iron is σ -bound to two cyclopentadienyl ligands. However, the stability of the compound in air and inability to undergo catalytic hydrogenation or Diels–Alder reactions convinced Ernst Fischer that the proposed structure was incorrect. Fischer proposed that all the six π -electrons of each cyclopentadienyl anion participate in the bonding to the iron(II) center which possesses an 18-electron configuration.¹⁸ In addition, Woodward and Wilkinson reported that the IR spectrum of the compound shows only one C–H stretching mode, indicating that all C–H bonds are identical with zero dipole moment.¹⁹ Dunitz confirmed this “sandwich structure” via X-ray diffraction studies in 1956 (Figure 2).²⁰ In a “ferric” nod to benzene, Woodward suggested the name *ferrocene*, which was quickly accepted worldwide. Today, compounds with the general composition $[\text{M}(\text{C}_5\text{H}_5)_2]$ are termed *metallocenes*.

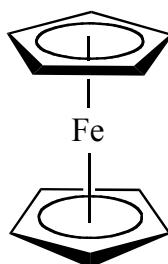


Figure 2. Structure of ferrocene, $(\text{C}_5\text{H}_5)_2\text{Fe}$.

The evolution of organometallic chemistry, notably of the transition metals, has revolutionized numerous disciplines of science and technology. The discovery of new

chemical compounds, unique structure and bonding modes, and unprecedented reactivity has provided the opportunity to explore their various applications in biological systems and industrial catalysis. The continual evolution of the field of organometallic chemistry certainly continues to hold a promising future.

1.3 Synthetic Techniques of Organometallic Compounds

Many organometallic compounds are air-sensitive and quite susceptible to oxidation. Therefore, such compounds should be handled under an inert atmosphere of argon or nitrogen. Nitrogen is more frequently used since it is less expensive than argon. However, nitrogen reacts with lithium at room temperature and several metal complexes at elevated temperatures,²¹ in which case argon is preferable. The solvents are usually dried and deoxygenated using reagents such as LiAlH₄, sodium-benzophenone stills, Na-K alloy, P₂O₅, or CaH₂. Among these reagents, sodium-benzophenone stills are beneficial in regards to having a visual indication that the solvent is thoroughly dried. For instance, the color of the solution turns purple in THF or green in hexane indicating the formation of the sodium-benzophenone ketyl radical and the exhaustion of water and oxidizing species. The thin layer of absorbed moisture on glassware is removed by placing it in the oven (~125 °C) overnight.²¹

Bench top manipulation of most organometallic compounds is properly performed using Schlenk lines (named after Prof. Wilhelm Schlenk, 1879 – 1943), which consists of an inert-gas glass manifold separated from a glass vacuum manifold using two-way Teflon stopcocks. The reaction vessels, known as Schlenk flasks, are connected to this dual manifold using a rubber hose. This permits repeated vacuum and refill of the inert

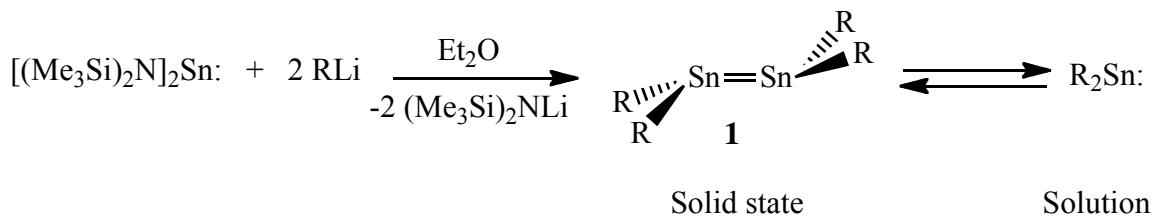
gas. In addition, an inert-atmosphere glove box is used to transfer air sensitive solid and liquid reagents, store air sensitive chemicals, and prepare samples for characterization.

Chemical compounds are often characterized by a combination of modern techniques such as nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, ultraviolet-visible (UV-vis) spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, elemental analyses (EA), and mass spectrometry (MS). However, single crystal X-ray crystallography is the predominant method that permits the unambiguous structural characterization of compounds in the solid-state.

1.4 Low-Valent Main Group Element-Element Bonds

The synthesis of low-valent, low-coordinate main group organometallic complexes containing element-element bonds has become an active area of research. This is due to the general interest in understanding the structure and bonding modes of these complexes. Prior to 1976, this field was largely stagnant due to experimental^{22,23} and theoretical studies^{24,25} that suggested multiple bonding for heavier elements ($n \geq 3$) was impossible. The so-called “double bond rule”,²⁶ proposed by Goubeau in 1957, stated that elements with principal quantum number (n) equal to or greater than three were unable to form multiple bonds. This rule was challenged by Lappert’s isolation of the first compound containing a tin-tin double bond (distannene), $R_2Sn=SnR_2$ ($R = CH(SiMe_3)_2$) **1** (Scheme 2).²⁷ In contrast to the planar geometry of C=C double bonds, **1** exhibited a trans-bent geometry with pyramidalization at the tin centers. The Sn–Sn bond length (2.76 Å) is slightly shorter than the Sn–Sn single bond (2.80 Å) but longer than the sum of Sn–Sn double bond covalent radii (2.60 Å). However, **1** was not stable in solution,

dissociating into stannylenes monomers as confirmed by UV-Vis and trapping experiments.



Scheme 2. Synthesis of distannene, $R_2Sn=SnR_2$ ($R = -CH(Me_3Si)_2$).

This landmark discovery provided a platform for further studies of low-valent element-element bonded species of the heavier p-block elements. Reports of the first disilene, $\text{Mes}_2\text{Si}=\text{Si}\text{Mes}_2$ ($\text{Mes} = 2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$),²⁸ diphosphene, $\text{Mes}'\text{P}=\text{PMes}'$ ($\text{Mes}' = 2,4,6\text{-}^t\text{Bu}_3\text{-C}_6\text{H}_2$),²⁹ and digermene, $\text{Dsi}_2\text{Ge}=\text{Ge}\text{Dsi}_2$ ($\text{Dsi} = \text{CH}(\text{Me}_3\text{Si})_2$),³⁰ contributed substantially to discussions on nature of multiple bonding. Additional studies have afforded homonuclear metal-metal double bonds (dimetallenes) of the group 13 (Ga ,³¹ In ³²), group 14 (Si ,³³ Ge ,^{34,35} Sn ,³⁵ Pb ^{36,37}), and group 15 elements (P ,³⁸ As ,³⁸⁻⁴⁰ Sb ,⁴¹ Bi ⁴²). Collectively, these studies hastened the demise of the dubious double bond rule.

The utilization of sterically demanding ligands was critical in the synthesis of these iconic molecules. The electronic properties of these ligands coupled with the considerable steric bulk, occupying a larger area around the metal coordination center, enhance the stability of these complexes. In particular, trimethylsilyl ((SiMe₃)₂CH), and terphenyl (C₆H₄R₂, R= alkyl, aryl) ligands have been frequently employed to stabilize many low-coordinate main group molecules.⁴³⁻⁴⁷ A notable structural feature of these species is the trans-bent geometry at the main group element center, and elongation of the multiple bonds upon descending the group.

Clearly, the classical σ - π bonding model for the elements carbon, nitrogen and oxygen does not apply to the heavier elements. This unusual characteristic of the heavier elements has been attributed to the increased stability of the singlet rather than the triplet form in going down a group.⁴⁸ The association of two singlet monomers would lead to considerable Pauli repulsion between the lone pairs. Due to the significant energetic cost needed to overcome the singlet-triplet energy gap, the monomers prefer to interact via a donor-acceptor arrangement of orbitals. For instance, in the heavier congeners of alkenes, a pair of electrons is donated from an sp^2 hybridized orbital of one metal atom to the empty p_z orbital of the second (Figure 3). Such interaction results in a trans-bent molecule pyramidalized at each metal center.

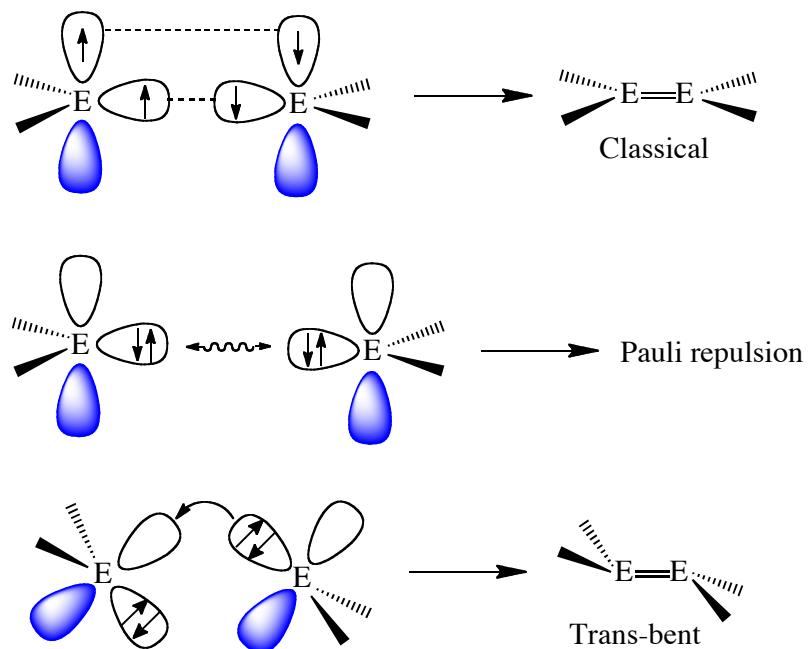


Figure 3. Triplet vs singlet interactions of element-element bonds.

An alternative approach attributes such geometry to the stronger π - σ orbital mixing due to reduced energy separation between these orbitals upon descending the group.⁴⁸ This orbital mixing weakens the π -orbital energy level, which in turn lengthens the bond

and increases the distortion (Figure 4). The degree of trans-bending is also affected by the electron donor or electron acceptor properties of the substituents on the metal center. Electron-withdrawing substituents increase the degree of π - σ^* interaction, which cause a significant trans-bending. On the contrary, electron-donating substituents cause much smaller deformations. These findings illustrate that the planar geometry of the second row elements is, in fact, the exceptional case and the trans-bent geometry represents the norm for the heavier doubly bonded main group complexes.

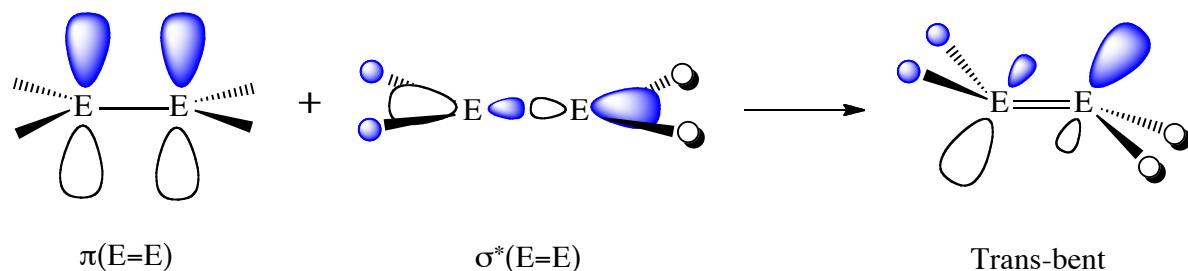
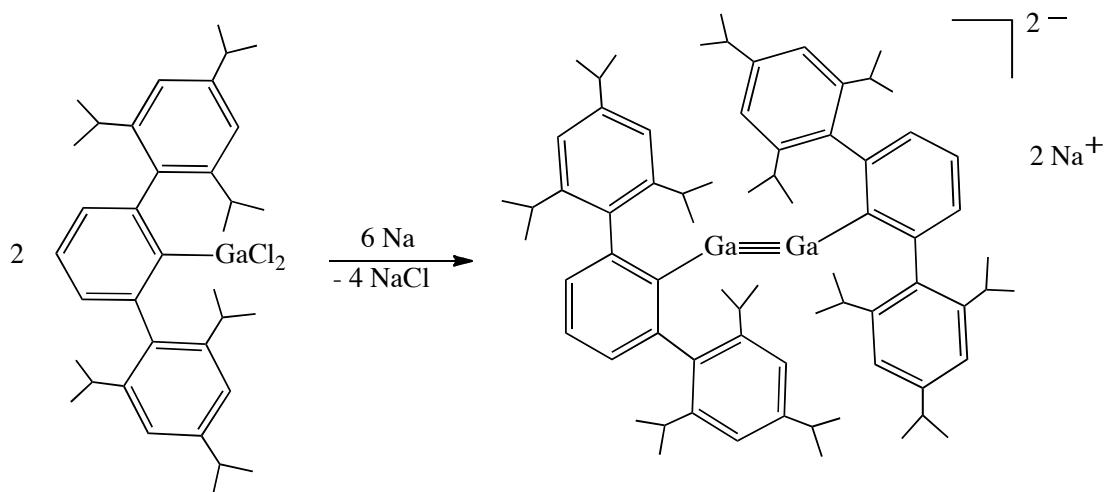


Figure 4. π - σ^* orbital mixing.

Homonuclear element-element triple bonds (dimetallynes) have also been reported for the group 13 (Ga^{49} , Al^{50}) and group 14 (Si^{51} , $\text{Ge}^{52,53}$, Sn^{54} , Pb^{37}) elements. The geometry of these molecules also exhibits a trans-bent geometry. The proposed bonding model indicates the presence of a donor-acceptor bond (similar to dimetallenes) and a weak p-p π -bond. However, the task of assigning the bond order for these molecules is not easily discernible. For instance, the first report of a compound of the form RPb-PbR ($\text{R} = 2,6\text{-}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{-})^{55}$) contained a Pb-Pb distance of 3.19 \AA , which is longer than the Pb-Pb single bond in diplumbane $\text{Ph}_3\text{Pb-PbPh}_3$ (2.84 \AA).⁵⁶ The authors suggested the presence of a Pb-Pb single bond with a lone pair of electrons at each lead center, which has been further supported by computational studies.⁵⁷

Among the group 13 elements, the first digallyne, $\text{Na}_2[\text{RGa}\equiv\text{GaR}]$ ($\text{R} = \text{-C}_6\text{H}_3\text{-2,6-}(\text{C}_6\text{H}_2\text{-2,4,6-}i\text{-Pr}_3)_2$), was prepared by Robinson via the sodium reduction of RGaCl_2 (Scheme 3).⁴⁹ The sodium atoms resided on either side of the $\text{Ga}\equiv\text{Ga}$ bond. Although the $\text{Ga}\equiv\text{Ga}$ bond was the shortest on record ($2.319(3)$ Å), the triple bond formulation was provocative due to the non-linear C–Ga–Ga–C backbone (C–Ga–Ga bond angles: $128.5(4)^\circ$ and $133.5(4)^\circ$) and the Ga–Ga bond length, which is only slightly shorter than a Ga–Ga single bond (2.440 – 2.790 Å).⁵⁸



Scheme 3. Synthesis of digallyne, $\text{Na}_2[\text{RGa}\equiv\text{GaR}]$ ($\text{R} = 2,6\text{-}(2,4,6\text{-}i\text{-Pr}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3\text{-}$).

It is pertinent to note that the C–Ga–Ga–C trans-bent geometry is a common phenomenon observed for multiply bonded heavier main group elements which has been supported by MO calculations and electron localization function (ELF) analysis.^{59–62} The ELF analysis, which differentiates between classical (slipped) and non-classical (unslipped) multiple bonds (Figure 5) revealed that the multiple bonding in both $\text{HC}\equiv\text{CH}$ and $\text{Na}_2[\text{HGa}\equiv\text{GaH}]$ is represented by a torso-type shape indicating similar bond order.

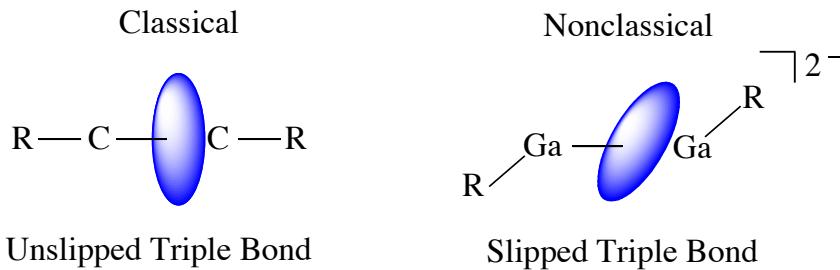


Figure 5. Unslipped vs slipped triple bond.

DFT studies on the digallyne, lacking only the isopropyl substituents on the phenyl ring, showed a NLMO/NPA bond order of 2.79, which is in agreement with the triple bond formulation. The $\text{Ga} \equiv \text{Ga}$ triple bond formulation can be elucidated by the bonding model shown in Figure 6. It is noteworthy that the compound that has been deemed as having an Al–Al triple bond, dialuminyne,⁵⁰ exhibits similar structural properties as the digallyne, which only reinforces the presence of a triple bond in digallyne.

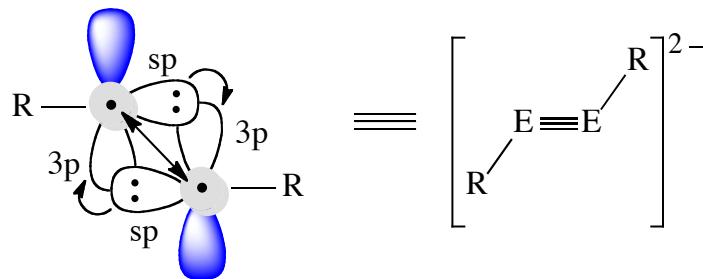


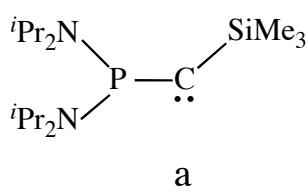
Figure 6. Triple bond model for heavier main group metallynes.

The metal centers of the numerous complexes discussed above are in the formal oxidation state of +1 or +2 since they have been isolated using (formally) anionic ligands. Recently, the utilization of neutral σ -donor ligands has provided a convenient means to isolate novel molecules containing homonuclear bonds in the formal oxidation state of zero. These types of molecules are particularly intriguing as they can serve as soluble allotropes of a given element through which further chemistry can be explored. One can envision several σ -donor ligands such as phosphines, amines, and ethers. However,

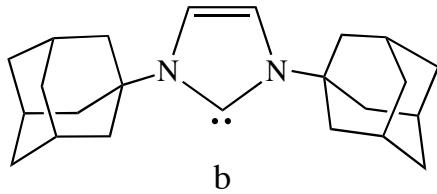
sterically encumbered carbenes (Section 1.5) have proven to be viable candidates due to their excellent σ -donor properties and their ability to shield a reactive center via bulky substituents. Our laboratory pioneered the utilization of a special class of organic bases, known as N-heterocyclic carbenes (NHCs), to stabilize highly reactive diatomic allotropes of the main-group elements (Si_2 ,⁶³ P_2 ,⁶⁴ As_2 ⁶⁵). The synthesis and reactivity of such molecules have afforded unique and often times unprecedented compounds.

1.5 Stable Carbenes

Carbenes are neutral, divalent two-electron donor carbon atoms surrounded by a sextet of electrons. The existence of carbenes as reactive intermediates was first reported by Curtis⁶⁶ (1885) and later by Staudinger⁶⁷ (1912). Such species were long considered to be too unstable to be isolated. By 1954, their presence was well-recognized when Doering proved the existence of dibromomethylene in cyclopropanation reactions via the addition of bromoform to an alkene.⁶⁸ Breslow⁶⁹ and Wanzlick⁷⁰ also realized the importance of amino substituents in stabilizing carbenes although they were unable to isolate such species. The first preparation of (phosphino)(silyl)carbenes was reported by Bertrand in 1988 (Figure 7a).⁷¹ Three years later, Arduengo ultimately reported the isolation of the first crystalline carbene (Figure 7b).⁷² These seminal discoveries led to the rapid development in the field of carbene chemistry. In particular, NHCs have been widely used as ancillary ligands in synthesizing transition metal-based catalysts.⁷³ Structural and thermochemical studies conducted by Nolan and coworkers indicated that NHCs are better σ -donor ligands than organophosphanes (PR_3).⁷⁴ The higher dissociation energy of these ligands compared to their phosphine congeners is an attractive feature since it avoids the use of excess ligand in catalytic reactions.



(Phosphino)(silyl)carbene



Adamantyl-substituted N-heterocyclic carbene

Figure 7. Examples of two early carbenes.

1.5.1 Stability of Carbenes

The ground-state spin multiplicity of carbenes can be either a singlet (spin paired) or a triplet (spin unpaired) (Figure 8). Singlet carbenes are bent in geometry. They contain an sp^2 hybridized carbene center with a vacant p orbital and a lone pair of electrons in the sp^2 hybrid orbital. Conversely, triplet carbenes are linear in geometry. They contain an sp hybridized carbene center and one electron in each pure p orbital.

The ground-state spin multiplicity determines the reactivity of carbenes. In the singlet state, carbenes can accept electrons via their empty p orbital (electrophilic center) as well as donate their lone pair of electrons from the sp^2 hybrid orbital (nucleophilic center). Therefore, their amphiphilic character allows for interaction with a nucleophile or an electrophile.⁷⁵ In the triplet state, carbenes are regarded as diradicals due to the presence of a single electron in each p orbital.⁷⁵ The electronic (inductive and mesomeric) and steric properties of the α -substituents determine the energy gap between the σ and p- π orbitals, which in turn determines the ground-state spin multiplicity. Specifically, an energy gap of \sim 40 kcal/mol favors the singlet state, while a value lower results in the triplet state.⁷⁶ Singlet carbenes are generally more stable and more widely used in organometallic chemistry than triplet carbenes.

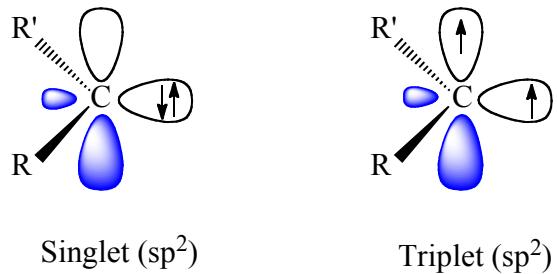


Figure 8. Electronic configuration of carbenes.

1.5.1.1 Inductive Effects

The electronegativity of the substituents on the carbene center influences its ground-state spin multiplicity. σ -electron-withdrawing substituents inductively stabilize the σ -nonbonding orbital of the carbon center by increasing its s character, while leaving the $p\pi$ unchanged.⁷⁵ This increased σ - $p\pi$ gap favors the singlet state (Figure 9, Type I). The reverse is true for σ -electron-donating substituents, which reduce the σ - $p\pi$ gap and favor the triplet state (Figure 9, Type II).

1.5.1.2 Mesomeric Effects

π -electron-donating substituents, such as -NR₂, -OR, and halides, increase the energy of the empty $p\pi$ orbital by interaction with the symmetric combination of the substituent lone pair of electrons.⁷⁵ Two new molecular orbitals, a bonding and a non-bonding, are formed with increased σ - $p\pi$ gap, which favors the singlet state (Figure 9, Type I). Alternatively, the symmetric combination of the vacant orbitals of the π -electron withdrawing substituents, such as -COR, -SOR, and -NO₂, interact with the p_y orbital perpendicular to the valance plane.⁷⁵ Since the p_x remains unaffected, the (p_x,p_y) degeneracy is broken also resulting in a singlet ground-state even though they are linear (Figure 9, Type II). Quasi-linear carbenes contain both π -donating and π -withdrawing substituents (Figure 9, Type III).⁷⁵ The lone pair of the π -donating substituents interacts

with the empty p_y orbital of the carbene, whereas the vacant orbital of the π-withdrawing substituents interact with the p_x orbital of the carbene center. These substituent effects both favor the singlet state.

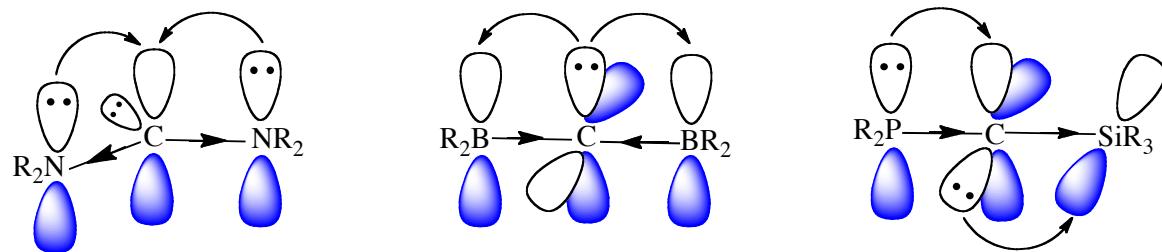


Figure 9. Inductive and mesomeric effects in carbenes.

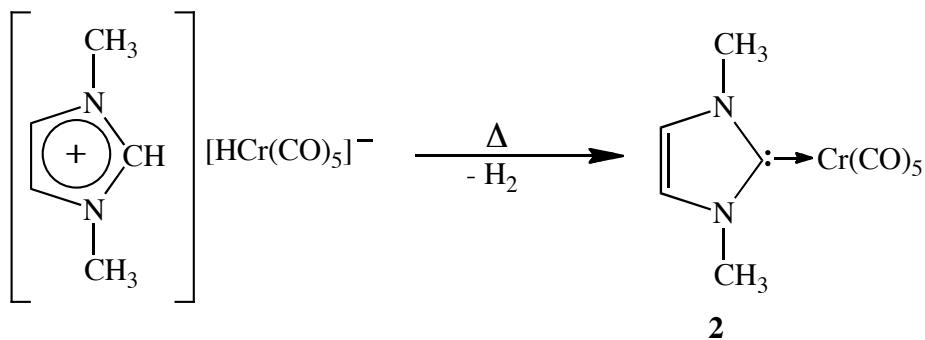
1.5.1.3 Steric Effects

The degree of steric bulk on the substituents also plays a role in favoring the singlet or triplet state, more so if the electronic effects are negligible. Increase in steric bulk leads to broadening of the carbene bond angle, favoring a linear geometry and promotes the triplet state.⁷⁵ However, less sterically encumbered substituents result in a smaller carbon bond angle (typically below 90°) and a larger σ-pπ gap favoring the singlet state.

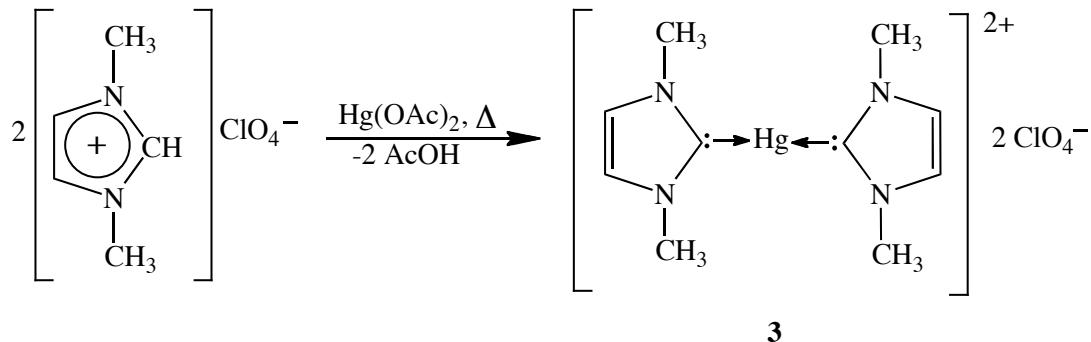
In recent years, NHC-stabilization of highly reactive main group molecules has become an active area of research.^{47,77-79} In particular, the landmark report of the first NHC-stabilized diatomic molecule (carbene-stabilized disilicon) invigorated this field.⁶³ Indeed, a recent theoretical study supports the superior σ-donor capabilities of NHCs compared to phosphines in stabilizing diatomic allotropes of the group 14 and 15 elements.⁸⁰ A second class of carbenes known as cyclic (alkyl)(amino)carbenes (CAACs) have also proven to stabilize highly reactive main group molecules.⁷⁸

1.5.2 N-Heterocyclic Carbenes

NHCs contain a neutral, divalent two-electron donor carbon atom stabilized in a five-membered imidazole ring. The chemistry of Fischer and Schrock type carbenes is well-known in transition metal chemistry.^{81,82} On the other hand, the chemistry of NHCs started to appear in the literature in the early 1960s. NHC containing chromium complex **2** (Scheme 4) and mercury complex **3** (Scheme 5) were reported by Wanzlick⁸³ and Öfele⁸⁴ by thermal extraction of hydrogen from imidazolium salts in the presence of metal containing precursors.



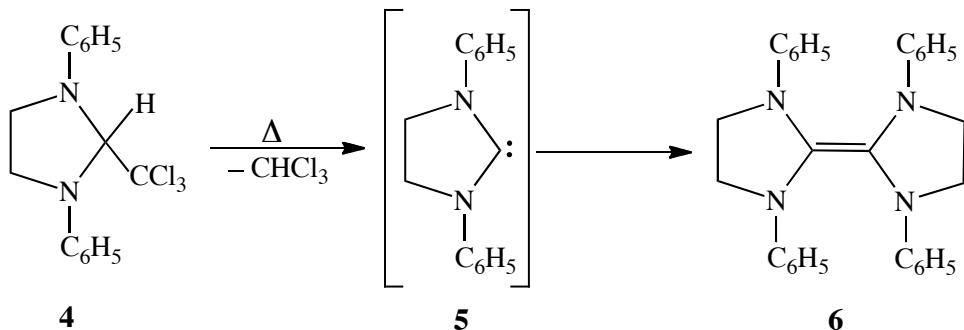
Scheme 4. Synthesis of NHC-chromium complex.



Scheme 5. Synthesis of NHC-mercury complex.

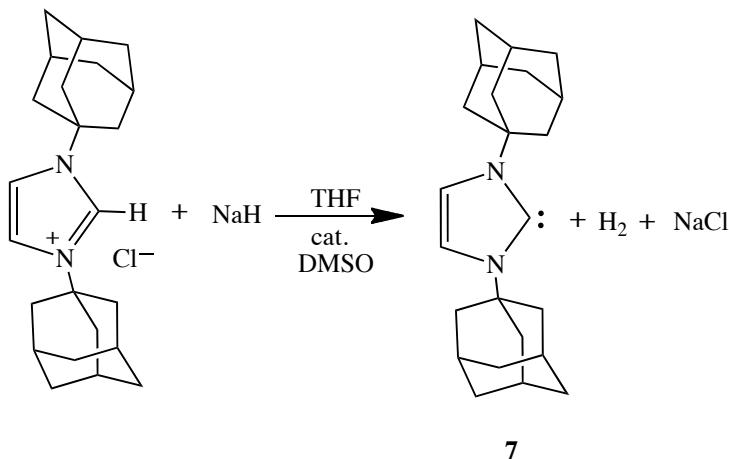
Subsequent attempts to isolate free NHCs were carried out by Wanzlick and coworkers who conjectured that 1,3-diphenylimidazolidin-2-ylidene, **5**, could be prepared from 1,3-dipheny-2-trichloromethyl-imidazolidine, **4**, by thermal elimination of

chloroform (Scheme 6).⁸⁵ However, the dimerized electron-rich olefin, **6**, was isolated. In addition, cross-coupling experiments suggested the absence of an equilibrium between **5** and **6**, although newer results by Denk suggest the contrary.⁸⁶



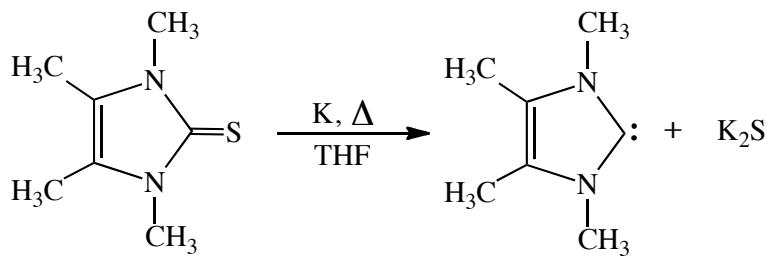
Scheme 6. NHC dimerization.

In 1970, Wanzlick's group suggested that deprotonation of the imidazolium salt with potassium tert-butoxide could afford the corresponding imidazole-2-ylidene, although attempts to isolate it were unsuccessful.⁸⁷ Arduengo and coworkers were ultimately able to isolate a stable crystalline NHC in 1991.⁷² The deprotonation of 1,3-di-1-adamantylimidazolium chloride with sodium or potassium hydride in catalytic amounts of dimethyl sulfoxide or *t*-BuOK afforded the corresponding free carbene, **7** (Scheme 7). Compound **7** is stable both in solution and the solid state and melts at 240–241°C without decomposition. Subsequent studies by Arduengo revealed that NHCs with less bulky aryl substituents are also isolable.⁸⁸ These results demonstrate that electronic factors take precedence over steric factors in stabilizing NHCs.



Scheme 7. Synthesis of the first crystalline NHC.

In 1993, Kuhn and coworkers reported a new approach to synthesize alkyl substituted NHCs. Desulfurization of alkyl substituted imidazole-2-thione with potassium in boiling THF yielded the corresponding imidazole-2-ylidene (Scheme 8). Although these alkyl substituted NHCs are significantly less bulky than the adamantyl substituted congeners, they are also quite stable in the absence of air and moisture.



Scheme 8. Synthesis of alkyl substituted NHC.

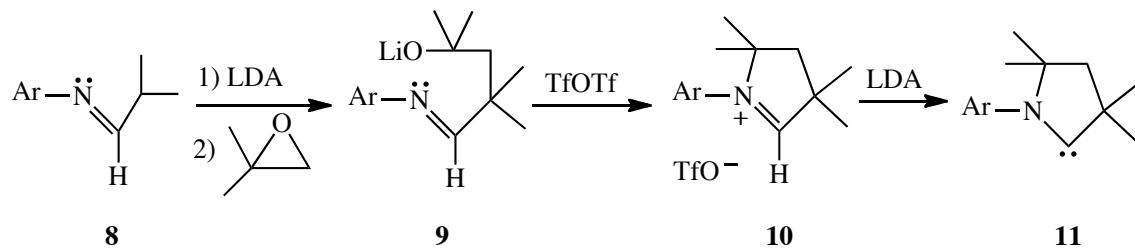
1.5.3 Cyclic (Alkyl)(Amino)Carbenes

In contrast to NHCs, cyclic (alkyl)(amino)carbenes (CAACs) contain only one nitrogen atom in the five-membered carbon heterocycle. The carbon atom α to the carbene center serves as a σ -electron donating group but not a π -donating group, which makes the carbene more electrophilic and nucleophilic than NHCs.⁷⁸ Quantum chemical calculations have shown that the singlet-triplet energy gap of the parent CAACs (46 kcal

mol^{-1}) is substantially smaller than that of the parent saturated NHCs (68 kcal mol^{-1}).⁸⁹

Consequently, CAACs are better σ -donors and π -acceptors than NHCs. Furthermore, the quaternary carbon α to the carbene center facilitates placement of a chiral center while also providing a flexible steric environment.⁸⁹

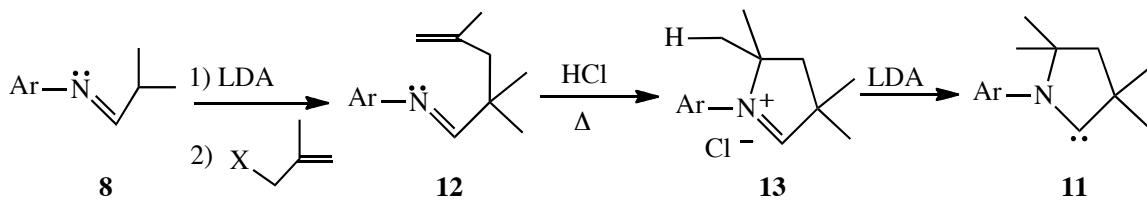
Bertrand and coworkers reported the first synthesis of CAACs in 2005 (Scheme 9).⁹⁰ Imine **8** was prepared from 2,6-diisopropylaniline and 2-methylpropanal. Deprotonation of **8** with lithium diisopropylamide (LDA) resulted in the aza-allyl anion, which induces the ring opening of 1,2-epoxy-2-methylpropane forming **9**. Addition of triflic anhydride ($[\text{CF}_3\text{SO}_2]_2\text{O}$) to **9** at -78°C afforded the triflate derivative, which forms the aldiminium salt **10** at room temperature. Deprotonation of **10** with LDA gave the CAAC **11**. A variety of substituents on the carbon at the carbene center and the nitrogen atom can be employed. However, the substituents on the former cannot be hydrides.



Ar = 2,6-diisopropylphenyl

Scheme 9. First synthetic route for preparation of CAAC.

Although the first strategy above led to the successful isolation of **11** in 48% yield, a second synthetic route was reported two years later, which gave **11** in 83% yield (Scheme 10). Deprotonation of **8** with LDA followed by addition of 3-bromo-2-methylpropene afforded **12**. The addition of HCl to **12** followed by heating to 50°C in acetonitrile gave **13**. Lastly, **13** was deprotonated with LDA to give CAAC **11**.



$\text{Ar} = 2,6\text{-diisopropylphenyl}$

Scheme 10. Alternate synthetic route for preparation of CAAC.

1.6 Carbene-Stabilized Highly Reactive Molecules

Over the past two decades, the utilization of carbene ligands has resulted in the isolation of a number of highly reactive main group molecules. Therefore, this section has been condensed to highlight recent achievements involving the group 13, 14, and 15 elements. The reactivity studies of these base-stabilized molecules continue to provide a means through which various low oxidation state molecules have become accessible. Common ligands that have been employed for this chemistry are depicted in Figure 10.

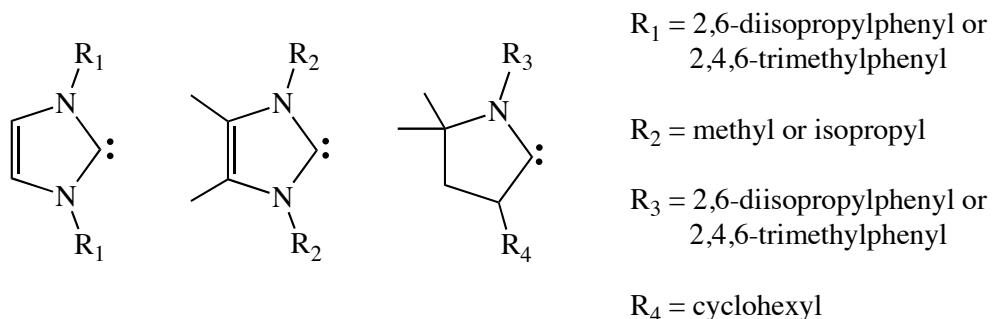


Figure 10. Common NHC ligands.

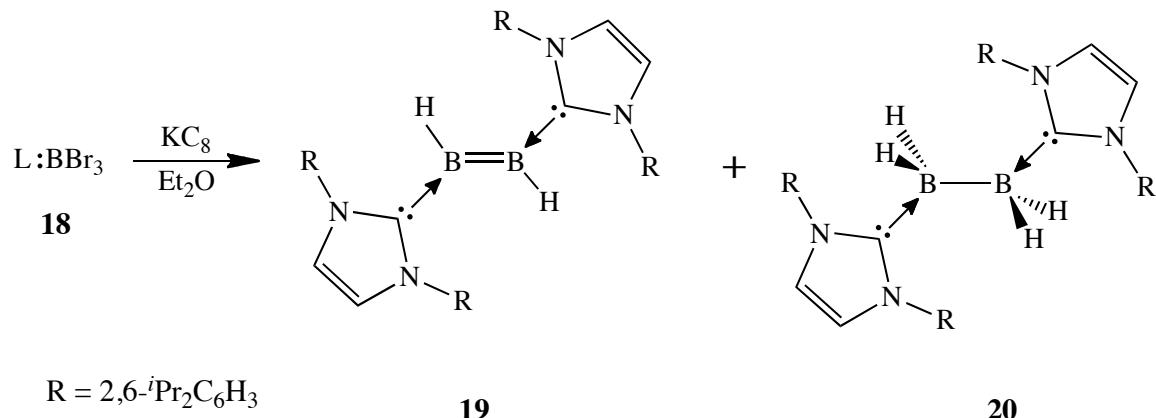
1.6.1 N-Heterocyclic Carbene-Stabilized Diborene

Due to the ‘electron poor’ nature of boron, it has been well-known to form clusters, rather than π -bonds, to relieve its electron deficiency. However, few homonuclear boron compounds, containing one- and two-electron π -bond, have been reported by power and coworkers. The two successive one-electron alkali metal reduction of tetraorganodiboron

compounds resulted in the first radical anion, $[\text{Mes}_2\text{BB}(\text{Mes})\text{Ph}]^{\bullet-}$ (**14**),⁹¹ containing a one-electron π -bond, and diborane dianions, $[\text{Mes}_2\text{B}=\text{B}(\text{Mes})\text{Ph}]^{2-}$ (**15**),⁹² containing a $\text{B}=\text{B}$ double bond. In addition, $[\text{Ph}(\text{Me}_2\text{N})\text{B}=\text{B}(\text{NMe}_2)\text{Ph}]^{2-}$ (**16**),⁹³ and $[\text{R}(\text{Me}_2\text{N})\text{B}=\text{B}(\text{NMe}_2)\text{R}]^{2-}$ ($\text{R} = \text{pyrrolyl, indolyl, carbazolyl}$) (**17**),⁹⁴ have also been reported. In order to synthesize neutral compounds containing a boron-boron double bonds, the “extra” two electrons will need to be supplied by neutral σ -donor ligands rather than alkali metals. In addition, these ligands will have to be sufficiently bulky to shield the boron center from undergoing further transformations. NHCs have been proven to be quite sufficient in this regard.

The potassium graphite (KC_8) reduction of L:BBr_3 (**18**) ($\text{L:} = :\text{C}\{\text{N}(2,6-\text{'Pr}_2\text{C}_6\text{H}_3)\text{CH}\}_2$) in diethyl ether (**18:KC**₈ = 1:5.4) afforded carbene-stabilized neutral diborene, $\text{L:(H)}\text{B}=\text{B}(\text{H}):\text{L}$ (**19**) and diborane, $\text{L:(H)}_2\text{B}-\text{B}(\text{H})_2:\text{L}$ (**20**) (Scheme 11).⁹⁵ The decreasing yield of **19** with increasing amounts of KC_8 demonstrates the significant impact of the reaction stoichiometry. Notably, a **18:KC**₈ ratio of 1:9 afforded only compound **20**. The presence of hydride groups in compounds **19** and **20** may be attributed to the rapid alkali-metal mediated abstraction of hydrogens from ethereal solvents.⁹⁶⁻⁹⁸ The boron atoms in **19** adopt a trigonal planar geometry and have a formal oxidation state of +1. Alternatively, the boron atoms in **20** have a formal oxidation state of +2 and reside in a tetrahedral environment. Not only is the $\text{B}=\text{B}$ bond distance in **19** (1.560(18) Å) significantly shorter than that in **20** (1.828 Å), but also shorter than the boron dianions **15** (1.636 Å), **16** (1.627 Å), **17** (1.566 – 1.59 Å), and comparable to the computed $\text{B}=\text{B}$ bond length for $\text{OC}(\text{H})\text{B}=\text{B}(\text{H})\text{CO}$ (1.590 Å).⁹⁹ Moreover, the difference in $\text{B}-\text{B}$ bond distance between **19** and **20** (0.27 Å), is comparable to the difference between ethane and ethene

(0.2 Å). The aluminum analogues of **20** have also been isolated by reducing L:AlH₃ with RMg–MgR (R = [(MesNCMe)₂CH]⁻).



Scheme 11. Synthesis of NHC-stabilized diborene **19** and diborane **20**.

The utilization of a less sterically encumbered ligand, L': (L': = :C{N(2,4,6-Me₃C₆H₂)CH}₂), has also afforded the corresponding diborene, **21**, and diborane, **22**.¹⁰⁰ A striking feature of **21** is its conformational flexibility shown by its three polymorphic structures: planar (**21a**), twisted (**21b**), and trans-bent (**21c**) (Figure 11). This may be attributed to the flat potential energy surface, packing effects in crystals, crystallization conditions, and the smaller size of the ligand.¹⁰⁰ While **19**, **21a**, and **21b**, adopt a trigonal-planar geometry, **21c** is the first example of pyramidal three-coordinate boron in an acyclic environment.¹⁰¹ While the B=B bond distances in **21a** (1.602(5) Å) and **21b** (1.584(2) Å) are comparable to that in **19**, the B=B bond distance in **21c** (1.679(9) Å) is about 0.1 Å longer. However, the Wiberg and NLMO/NPA B–B bond indices of **21c** (1.445 and 1.515 respectively) are comparable to those in **19** (1.408 and 1.656 respectively) indicating that the electronic structure, rather than the bond distances, determines the nature of the multiple bond.⁶¹

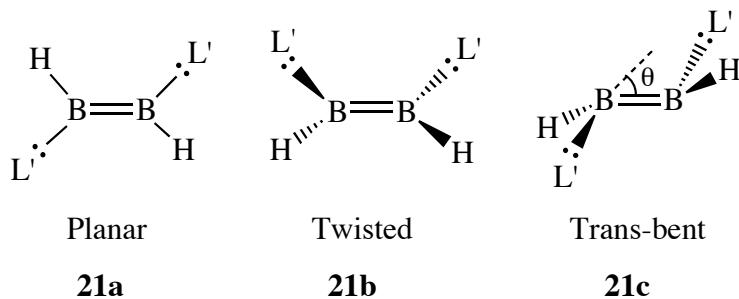


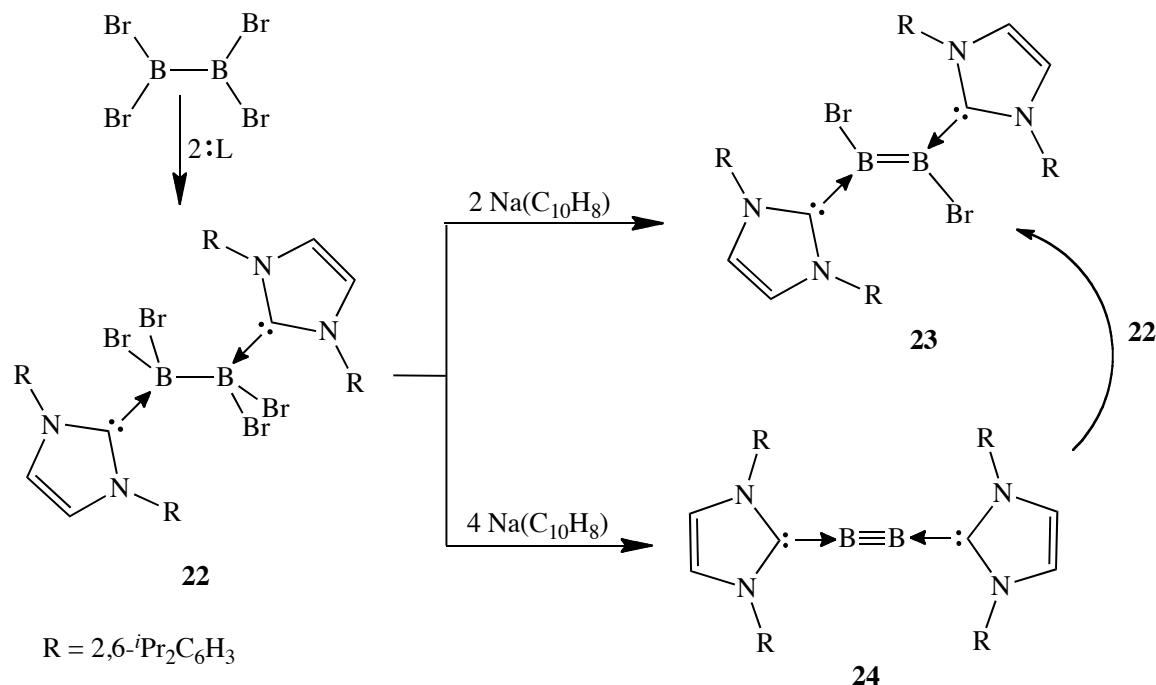
Figure 11. Polymorphic structures of diborene.

1.6.2 N-Heterocyclic Carbene-Stabilized Diboryne

Although there were reports of dianionic dialuminyne⁵⁰ and digallyne⁴⁹ of the form $\text{RE}\equiv\text{ER}^{2-}$ ($\text{E} = \text{Al}, \text{Ga}$), homonuclear triple bond among the lighter element, boron had long remained elusive under ambient conditions. However, the reaction of laser-vaporized boron atoms in the presence of CO had afforded $\text{L}: \text{B}\equiv\text{B}: \text{L}$ ($\text{L} = \text{CO}$) albeit at very low temperatures (8K).¹⁰² In addition, $\text{L}': \text{B}\equiv\text{B}: \text{L}'$ ($\text{L}' = \text{BO}^-$) and its lithium salt has been identified in the gas phase via photoelectron spectroscopy.¹⁰³ Quantum chemical calculations have also predicted the possibility of stabilizing a neutral $\text{B}\equiv\text{B}$ triple bond,¹⁰³⁻¹⁰⁷ which encouraged chemists to pursue its isolation at room temperature. Braunschweig ascribed the formation of the parent diborenes, **19** and **21**, to a slow boron-boron coupling step, which could likely form a boron-based radical intermediate.¹⁰⁸ This radical species can easily abstract hydrogens from the solvent rather than forming a boron-boron triple bond. Accordingly, it was reasonable to hypothesize that reduction of a molecule with a performed boron-boron single bond would make it much more probable to form a boron-boron triple bond.

Indeed, the addition of two equivalents of $\text{L}: (\text{L}: = :\text{C}\{\text{N}(2,6-\text{iPr}_2\text{C}_6\text{H}_3)\text{CH}\}_2)$ to tetrabromodiborane, B_2Br_4 , afforded the NHC-stabilized diborane, $\text{L}:(\text{Br}_2)\text{B}-\text{B}(\text{Br}_2):\text{L}$

(22) (Scheme 12).¹⁰⁸ Reduction of **22** with two and four equivalents of sodium naphthalenide, Na(C₁₀H₈), afforded neutral bis(carbene)-stabilized dibromodiborene, L:(Br)B=B(Br):L (**23**), and NHC-stabilized diboryne, L:B≡B:L (**24**) respectively. Notably, the combination of equimolar amounts of **22** and **24** resulted in complete conversion to **23** as monitored by ¹¹B NMR. Compound **24** is quite stable up to 234 °C under inert atmosphere.



Scheme 12. Synthesis of NHC-stabilized diborene **23** and diboryne **24**.

The trigonal planar geometry and B=B bond distance of **23** (1.546 Å) compares well to that in parent diborenes **19**, **21a**, and **21b** and to the computed values for OC(H)B=B(H)CO (1.590 Å)⁹⁹ and HB=BH (1.498 – 1.515 Å).¹⁰⁹ Compound **24** exhibits a linear arrangement of B≡B core, which is consistent with theoretical predictions.^{106,107}

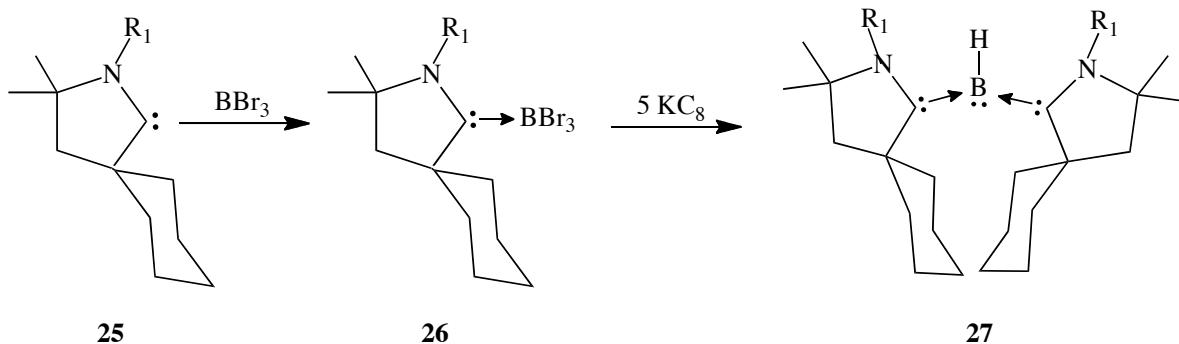
The B≡B bond distance of **24** is 1.449 Å in accordance with computational (1.439 – 1.481 Å)¹⁰³⁻¹⁰⁷ and experimental reports in matrix isolation (1.453 – 1.468 Å)¹⁰² and

photoelectron spectroscopy ($1.478 - 1.530 \text{ \AA}$).¹⁰³ In addition, the $\text{B} \equiv \text{B}$ bond distance in **24** is shorter than that of **23** by 0.097 \AA . The ^{11}B NMR signals show a continual downfield shift with decreasing coordination number (**22** = -4.8 ppm , **23** = 20 ppm , **24** = 39 ppm). This remarkable discovery places boron among the elite main group elements that contain a triple bond.

1.6.3 Cyclic (Alkyl)(Amino)Carbene-Stabilized Parent Borylene

Borylenes are monocoordinated boron species with a lone pair of electrons ($\text{R-B}:$), and are isoelectronic with carbenes and amines.¹¹⁰ These species have long been known as fleeting intermediates, which were only characterized by IR spectroscopy in solid argon matrices at low temperatures.^{111,112} Although transition-metal coordinated borylenes have been characterized by X-ray diffraction studies, attempts to isolate free borylenes had remained unsuccessful.¹¹³ The two vacant p-orbitals and the lone pair of electrons promote the reaction of borylenes with nucleophiles and electrophiles, and consequently attribute to their high reactivity. While the presence of NHC-coordinated parent borylene had been characterized by trapping experiments,¹¹⁴ the isolation of CAAC-stabilized parent borylene has now enabled its full characterization under ambient conditions.¹¹⁰

Compound **26** was prepared by reaction of L: (L: = cyclic (alkyl)(amino)carbene (CAACs) **25**) with BBr_3 in hexane. The reduction of **26** with five equivalents of potassium graphite (KC_8) afforded a CAAC-stabilized parent borylene **27** in moderate yield (33%) (Scheme 13). Alternatively, the reduction of to a 1:1 mixture of **25** and **26** also afforded **27** albeit low yield (8%).

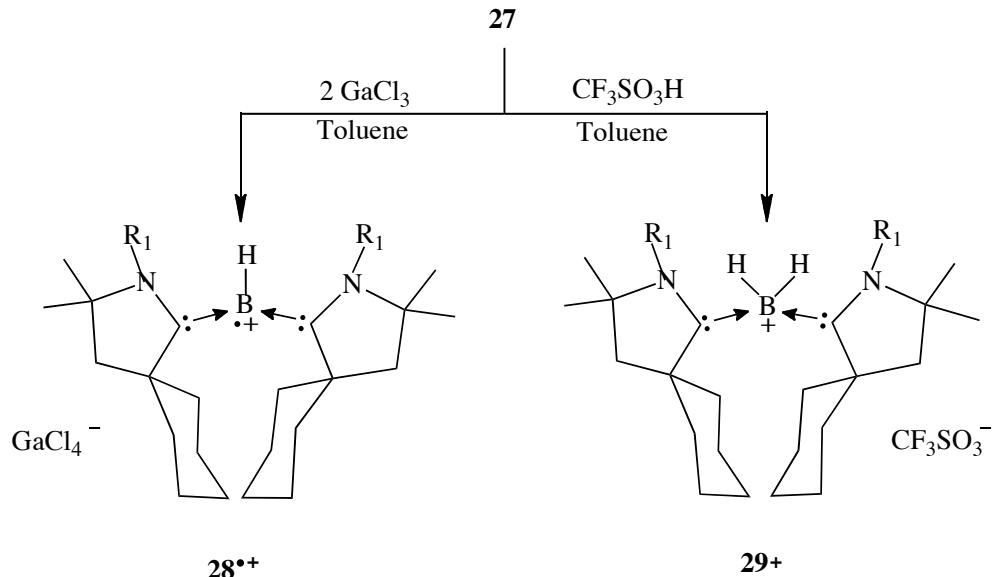


Scheme 13. Synthesis of CAAC-stabilized parent borylene **27**.

The three-coordinate boron atom in **27** adopts a trigonal planar geometry. The presence of hydrogen coordinated to the boron center was confirmed by infrared absorption at 2455 cm^{-1} . In addition, the B–C bond lengths (1.517 and 1.516 \AA) are halfway between that of a B–C single bond (1.59 \AA)⁹⁵ and a B=C double bond (1.42 \AA)¹¹⁵ indicating electron resonance between the carbene carbon and the boron center. Contrary to tricoordinate boron(III) compounds that are lewis acidic, **27** is in the formal oxidation state of +1 and can serve as a Lewis base. Accordingly, the addition of two equivalents of gallium(III) chloride afforded a boron radical cation, $[\mathbf{28}^+]\text{GaCl}_4^-$, which is a rare example of boron radicals and boron molecules in the +2 oxidation state (Scheme 14). The decreased π -back donation from boron to carbene in $[\mathbf{28}^+]\text{GaCl}_4^-$ is indicated by the longer B–C and shorter C–N bonds (1.583 \AA and 1.357 \AA respectively) in comparison to those in **27** (1.517 \AA and 1.377 \AA respectively).

Although compound **27** can serve as a Lewis base, its coordination to a bulky Lewis acid (trimethylsilyl or methyl-trifluoromethanesulfonate) is hampered due to the steric protection of the CAACs. Alternatively, treatment of **27** with triflic acid resulted in a tetracoordinate boronium cation, $(\mathbf{29}^+)\text{CF}_3\text{SO}_3^-$. The absence of π -back donation is indicated by yet a longer boron-carbon and shorter carbon-nitrogen bonds in $\mathbf{29}^+$ (1.610 \AA

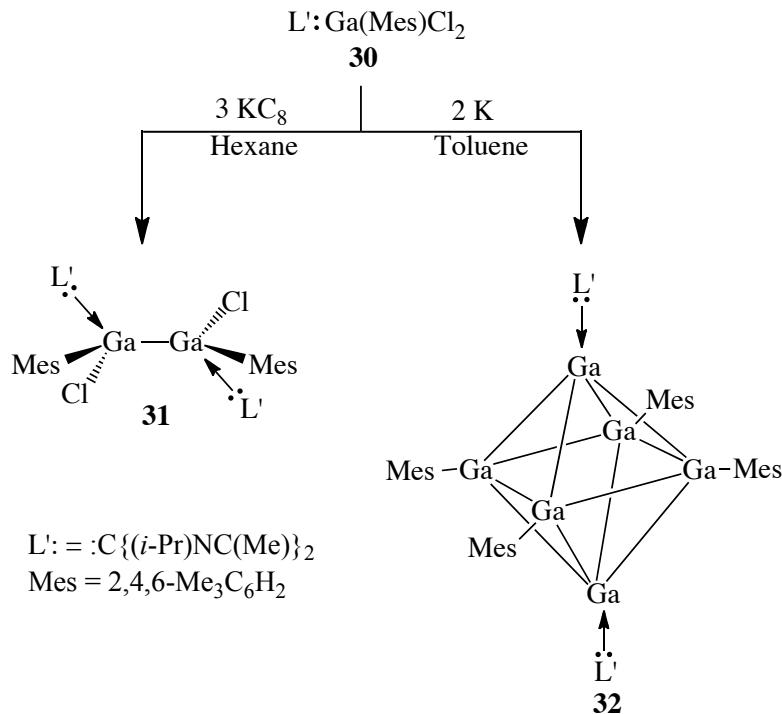
and 1.308 Å respectively). Compound $(\mathbf{29}^+){\text{CF}_3\text{SO}_3^-}$ can also be deprotonated by sodium ethoxide to give **27**. Not only are compounds of type **27** isoelectronic with amines and phosphines, but are also less electronegative, which makes them better electron donors.



Scheme 14. Oxidation and protonation CAAC-stabilized parent borylene **27**.

1.6.4 N-Heterocyclic Carbene-Stabilized Ga₆ Octahedron

The alkali metal mediated reduction of NHC-coordinated GaCl₃ has also been explored. Although the reduction of L:GaCl₃ (L: = :C{N(2,6-*i*-Pr₂C₆H₃)CH}₂) did not afford the expected Ga≡Ga triple bond, the utilization of a less sterically encumbered ligand, L': (L': = :C{(i-Pr)NC(Me)}₂), coordinated to Ga(Mes)Cl₂ (Mes = 2,4,6-Me₃C₆H₂) resulted in two quite distinct molecules. The reduction of L':Ga(Mes)Cl₂, **30**, with KC₈ (**30**:KC₈ = 1:3) in hexane afforded a pale-yellow (L':Ga(Mes)Cl)₂ dimer **31** (Scheme 15).¹¹⁶ Alternatively, the reduction of **30** with potassium metal (**30**:K = 1:2) in toluene afforded ruby-red crystals of L':Ga[Ga₄Mes₄]Ga:L' cluster, **32**, which contains six gallium atoms arranged in an octahedral fashion. Notably, **32** represents the first example of a neutral aromatic Ga₆ octahedron.



Scheme 15. Synthesis of NHC-stabilized digallane **31** and Ga₆ octahedron **32**.

Each gallium atom in **31** has a formal oxidation state of +2 and adopts a distorted tetrahedral geometry. The Ga–Ga bond length of **31** (2.447 Å) compares well with those in the four coordinate gallium(II) amidinate complexes [GaI(MeCNAr)]₂ (2.430 Å) and [GaI(HC(NAr)]₂ (2.452 Å).¹¹⁷ The two gallium(0) atoms at the axial position are each coordinated to a carbene ligand, whereas the four gallium(I) atoms at the equatorial position are each coordinated to a mesityl group. Although the arrangement of the gallium atoms is similar with Ga₆Cp₆ (Cp = Me₅C₅),¹¹⁸ the latter does not contain metal-metal bonds and cannot be considered a cluster. A second compound that contains six gallium atoms, Ga₆R₆ (R = SiMe(SiMe₃)₂),¹¹⁹ was described as a folded Ga₆ chair with 12 skeletal electrons, also indicating its non-octahedral geometry. On the contrary, **32** has 14 skeletal electrons which is consistent with Wade-Mingos rules^{120,121} and corresponds to a *closو* configuration. The difference in formal oxidation state between the Ga atoms

(+1 for equatorial and +2 for axial) results in a tetragonal compression of the Ga₆ octahedron.¹²²

1.6.5 N-Heterocyclic Carbene-Stabilized Disilicon

Since the first report of the structurally characterized molecule containing silicon-silicon double bond (disilene),²⁸ numerous low-valent silicon compounds have been isolated utilizing sterically demanding ligands.^{47,123} Disilenes of the form R₂Si=SiR₂ and disilynes of the form RSi≡SiR contain an Si₂ core in the formal oxidation state of +2 and +1 respectively. These species were isolated using formally anionic ligands. Recently, our laboratory introduced a new class of diatomic silicon molecules that retain a formal oxidation state of zero. Such species are quite intriguing, as they would represent soluble allotropes of elemental silicon through which further low-oxidation state molecules can be accessed. The choice of ligand and coordination number are critical factors in synthetically approaching homonuclear diatomic silicon compounds (Figure 12).

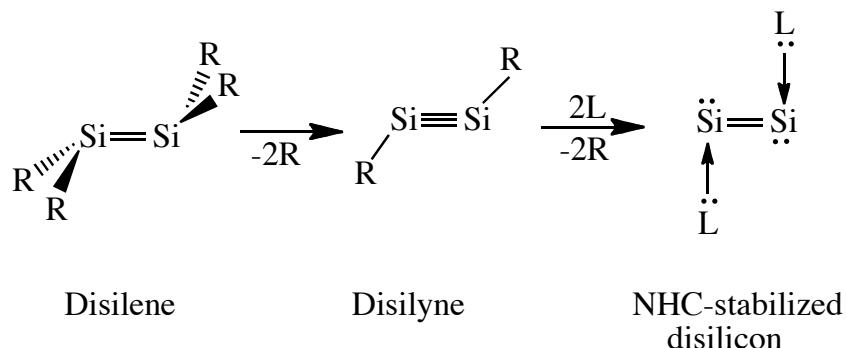
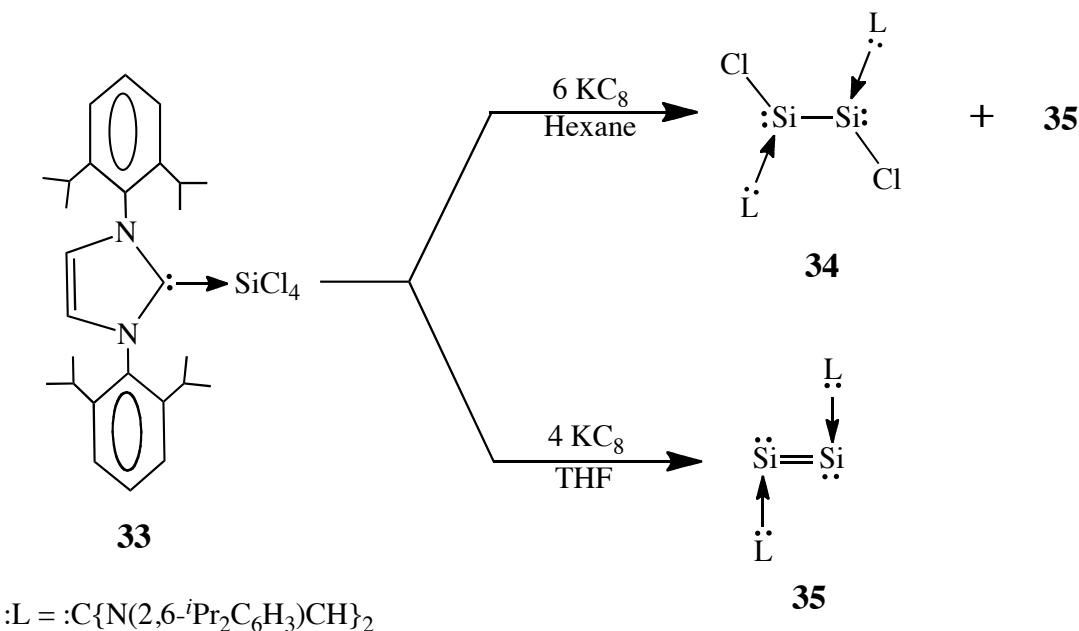


Figure 12. Conceptual progression from disilene to disilyne to carbene-stabilized disilicon of low-valent silicon-silicon compounds.

The first example of a homonuclear diatomic molecule, L:Si=Si:L **35** (L: = :C{N(2,6-^tPr₂C₆H₃)CH}₂) in the formal oxidation state of zero, was prepared in a series

of two steps.⁶³ The hypervalent precursor, L:SiCl₄ **33**, was prepared upon addition of SiCl₄ to a mixture of L: in hexane. The potassium graphite reduction of **33** in THF (**33**:KC₈ = 1:4) afforded dark-red crystals of **35** in 23.2% yield (Scheme 16). Alternatively, the reduction of **33** in hexane (**33**:KC₈ = 1:6) afforded a NHC-stabilized bis-silylene, L:(Cl)Si-Si(Cl):L **34**, as orange-red crystals accompanied by **35**.



Scheme 16. Synthesis of NHC-stabilized bis-silylene **34** and disilicon **35**.

The Si=Si bond distance in **35** (2.229 Å) is similar to the computed (2.249 Å)¹²⁴ and experimental (2.246 Å)¹²⁵ bond distances of Si₂. Furthermore, it compares well to the computed Si=Si bond distance in OC:Si=Si:CO (2.130 Å, B3LYP).¹²⁶ The Wiberg bond index (WBI) of 1.73 also supports the presence of a Si=Si double bond. The Si–C bond length (1.927 Å) compares well with the Si–C bond distance in **33**. The planes of the imidazole rings of the NHCs is perpendicular to the Si=Si vector (N–C–Si–Si torsion angle = 91.01°). The non-linear C–Si–Si–C linkage and the long C–Si bonds distances support the absence of a C–Si double bond and is consistent with a zero oxidation state

formulation at the silicon atoms. Contrary to the previously synthesized three-coordinate disilenes, which exhibit a trigonal pyramidal or planar geometry, **35** is two-coordinate with a *trans*-bent geometry around the Si₂ core (C-Si-Si bond angle = 93.57°). These structural features are in accordance with weak hybridization between the 3s and 3p orbitals of silicon atoms. This is consistent with predominantly 3p-character of the Si=Si bonding orbitals and predominantly 3s-character silicon lone-pair molecular orbitals according to NBO analysis. This report ignited the search of additional homonuclear bonds of the heavier main group elements in the zero oxidation state.

Carbene-stabilized digermanium (**37**)¹²⁷ and carbene-stabilized ditin (**38**)¹²⁸ of the form L:E=E:L (E = Ge, Sn) have also been prepared by Jones and coworkers upon reduction of L:ECl₂ (**36**) using RMg(I)-Mg(I)R (R = [N(Mes)CMe]₂CH). Compounds **37** and **38** are also isostructural to **34**. The carbene resonance in ¹³C{¹H} NMR spectrum shows a downfield shift in going down the group (Si₂ = 196.3 ppm, Ge₂ = 203.3 ppm, and Sn₂ = 210.3 ppm) all of which are upfield compared to free carbene (L: = 220.6 ppm).⁸⁸ This trend indicates a weaker interaction of the carbene with E (E = Si, Ge, Sn) upon descending the group.¹²⁸ In addition, the decreasing yield of the diatomic molecule (Si = 23.2 %, Ge = 20%, and Sn = 5%) indicates a weaker stability of the diatomic core upon descending the group, making it increasingly difficult to isolate heavier diatomic species. It is pertinent to note that a carbon(0) atom coordinated to two NHCs, C(NHC)₂, “carbodicarbene”,^{129,130} has also been synthesized and is in agreement with theoretical predictions.^{131,132} In addition, recent computational studies suggest a linear arrangement of NHC-stabilized dicarbon containing carbon-carbon and carbon-carbene double bonds.¹³³

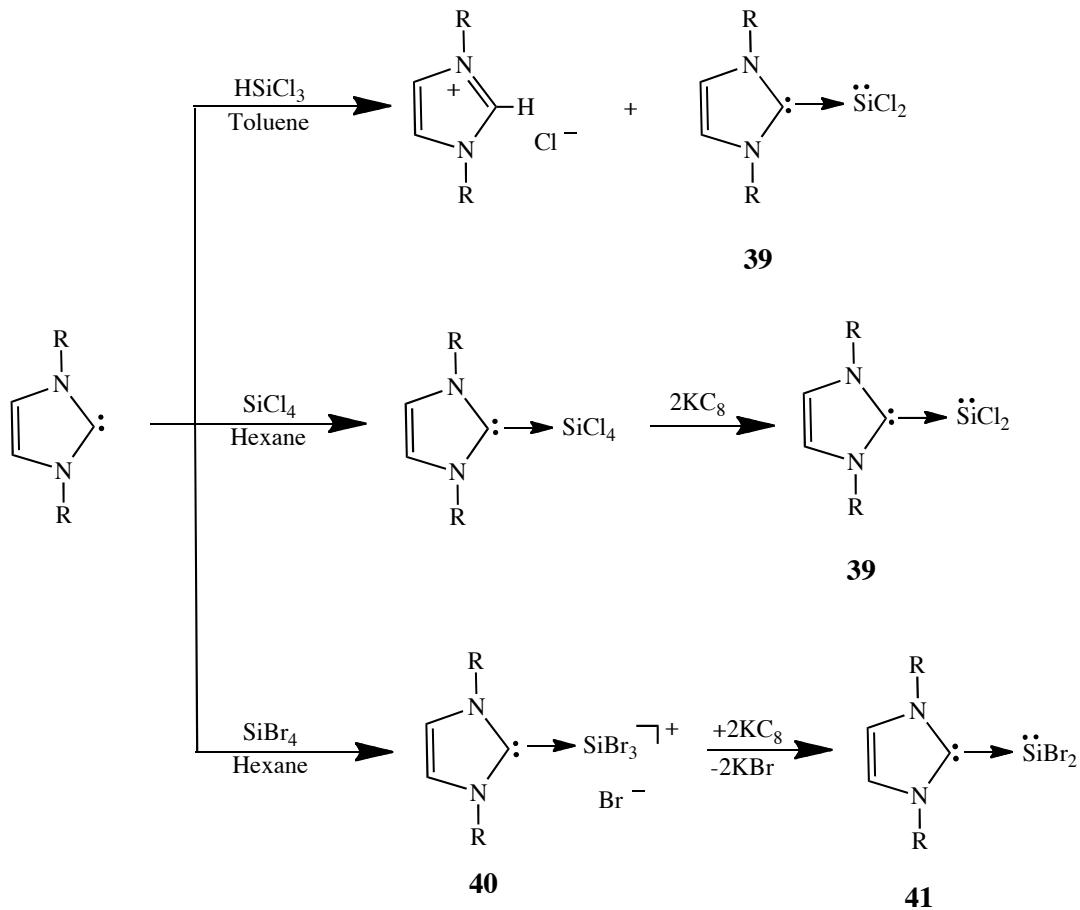
1.6.6 N-Heterocyclic Carbene-Stabilized Silylenes

Although all of the group 14 elements can undergo sp^3 hybridization to form a four-coordinate molecule, the stability decreases with increasing molecular weight. This is due to the increased resistance of the outermost s electrons to participate in bonding, a property known as the “inert pair effect”.¹³⁴ Consequently, two-coordinate germanium, tin, and lead, are much more prevalent than their silicon congener. In particular, lead tetrachloride readily decomposes to lead dichloride and chlorine gas above 50 °C.¹³⁴ In contrast, the chemistry of silicon is dominated by its preference to form four-coordinate compounds. Two-coordinate silicon compounds, known as silylenes, are known to exist as reactive intermediates.¹³⁵ Thermochemical studies of silicon dihalides have shown that such species disproportionate into elemental silicon and $SiCl_4$ at room temperature.¹³⁶⁻¹³⁸

Jutzi and coworkers reported the first stable silylene, decamethylsilicocene, in 1986.¹³⁹ N-heterocyclic silylene, with a silicon atom instead of carbon in NHCs, was subsequently reported by West and coworkers in 1994.¹⁴⁰ Several other cyclic silylenes¹⁴¹⁻¹⁴³ and a dialkylsilylene¹⁴⁴ have also been reported. However, the isolation of stable silicon dihalides that are stable at room temperature had remained elusive due to their rapid transformation into polymeric perhalopolysilanes, $(SiX_2)_n$.¹⁴⁵ Although these polymeric species were structurally characterized by West and coworkers,¹⁴⁶ the isolation of monomeric halosilylenes had long remained a challenge.

In 2009, Roesky demonstrated that NHCs are capable of stabilizing these monomeric halosilylenes under ambient conditions. The reductive elimination of HCl upon adding trichlorosilane to two equivalents of NHC ($L:$) $L: = :C\{N(2,6-\text{i-}Pr_2C_6H_3)CH\}_2$) afforded **39** in 79% yield (Scheme 17).¹⁴⁷ Alternatively, **39** was also prepared from the reaction of

two equivalents of KC_8 with L:SiCl_4 in 48% yield. Filippou reported a second dihalosilylene, **41**, in a series of two steps.¹⁴⁵ The addition of one equivalent of L: to SiBr_4 resulted in an ionic compound, $[\text{L:SiBr}_3]\text{Br}$ **40**. Treatment of **40** with two equivalents of KC_8 afforded **41** in 48% yield.



Scheme 17. Syntheses of NHC-stabilized dihalosilylenes **39** and **41**.

The crystal structures of **39** and **41** show trigonal pyramidal geometry about the silicon atoms. In addition, the sum of the bond angles at **39** and **41** are 289.7° and 292.7° , respectively. The Si–C bond distance in **39** (1.985 \AA) and **41** (1.989 \AA) are shorter than that in silylene–carbene adducts (2.162 \AA),¹⁴⁸ but longer than those in Si=C of silenes (1.702 \AA).¹⁴⁹ This indicates a strong C–Si donor acceptor bond wherein the carbene donates a lone pair of electrons into the vacant p-orbital of the silicon. The bond

dissociation energy of **41** (123.7 kJ mol⁻¹) is similar to that found in H₃N:BH₃ (118.4 kJ mol⁻¹),¹⁵⁰ which also supports the strong Si–C bond. The ²⁹Si NMR of **39** (19.06 ppm) and **41** (10.9 ppm) in C₆D₆ are similar to that in (PhC(*t*BuN)₂)SiCl (14.6 ppm).¹⁵¹ Notably, the ²⁹Si NMR of **41** in solution (10.9 ppm) and the solid state (15.8 ppm) are comparable indicating the similar structure of **41** in the solution and solid state. The isolation of dihalosilylenes has provided a means to study their reactivity at room temperature. Recent results have been summarized by Roesky.¹⁵²

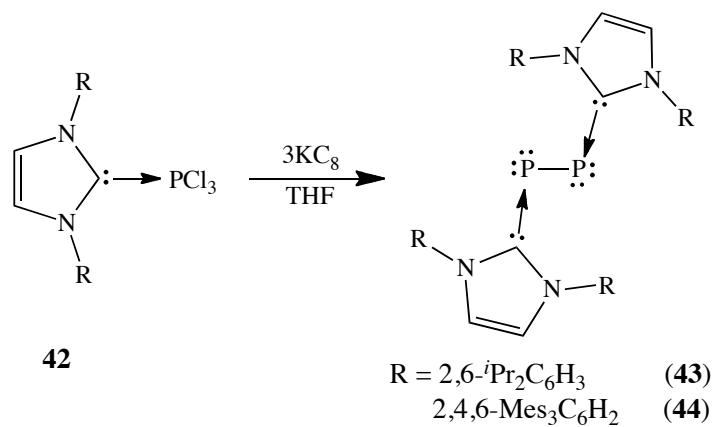
1.6.7 N-Heterocyclic Carbene- and Cyclic (Alkyl)(Amino)Carbene-Stabilized Diphosphorus

In contrast to its lighter congener nitrogen, phosphorus exhibits diverse allotropy: white, red, and black. The pyrolysis of white phosphorus (P₄) liberates the highly reactive gaseous allotrope P₂.¹⁵³ The bond dissociation energy of P₂ (109 kcal mol⁻¹) is significantly less than that of N₂ (232 kcal mol⁻¹).¹⁵⁴ In 2006, Cummins and co-workers reported the mild thermal extrusion of P₂ from niobium diphosphaazide complexes, which was captured by organic substrates.¹⁵⁵ The utilization of carbenes to stabilize P₂ has now provided the opportunity to explore its chemistry under ambient conditions.

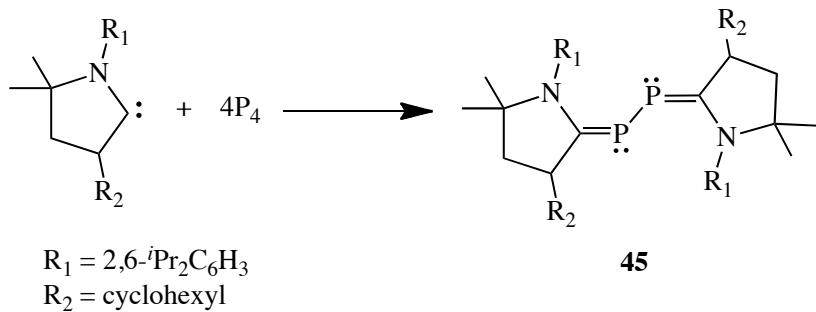
The potassium graphite reduction of L:PCl₃ **42** in THF afforded carbene-stabilized P₂ compounds L:P–P:L **43** (L: = L¹: = :C{N(2,6-ⁱPr₂C₆H₃)CH}₂) and **44** (L = L² = :C{N(2,4,6-Me₃C₆H₂)CH}₂) in moderate yield (56.6% and 20.7% respectively) (Scheme 18).⁶⁴ In addition, Bertrand and coworkers isolated CAAC (L') stabilized P₂, L':P–P:L' **45**, by carbene-induced fragmentation of P₄ (12% yield) (Scheme 19).¹⁵⁶

While compound **43**, has C_i symmetry and a trans-bent geometry (C–P–P–C torsion angle = 180°), **44** exhibits a gauche conformation (C–P–P–C torsion angle 134.1°). In

addition, computational studies on the simplified model, **43-H**, indicates a C₂ minimum (C–P–P–C torsion angle = 98.6). The decreasing torsion angle with decreased steric bulk of the ligands demonstrates the significant role of the ligand in the conformation of the P₂ molecule. The P–P single bond distances of **43** (2.205 Å), **44** (2.189 Å), and **45** (2.184 Å) compare well to that in P₄ (2.21 Å). The C–P–P bond angles of **43** and **44** (103.2 and 102.6 Å respectively) are comparable to that in **45** (105.1 Å). The P–C bond distance in **43** and **44** (1.750 and 1.754 Å respectively) are between the P=C double bond length in nonconjugated phosphaalkenes (1.65 – 1.67 Å) and the computed P–C single bond distance in H₃C–P=P–CH₃ (1.87 Å)⁴⁷ but 0.03 Å longer than that in **45** (1.719 Å).



Scheme 18. Synthesis of NHC-stabilized L:P-P:L **43** and **44**.



Scheme 19. Synthesis of CAAC-stabilized L':P-P:L' 45.

Two canonical forms, bis-phosphinidene (**A**) and bis-phosphaalkene (**B**), can be used to describe the bonding in **43**, **44**, and **45** (Figure 13). The high-field ^{31}P NMR of **43**

(−52.4 ppm) and **44** (−73.6 ppm) and relatively long P–C bond distances (1.75 Å) suggest that **43** and **44** are best represented as type **A**. In contrast, the low-field ^{31}P NMR ($\delta = +59.4\text{ ppm}$), similar to that in diphosphabutadienes (34 to 54 ppm), and the short P–C bond distance (1.719 Å) of **45** imply that it favors type **B** formulation. These parameters are in agreement with the higher electrophilicity CAACs than NHCs.

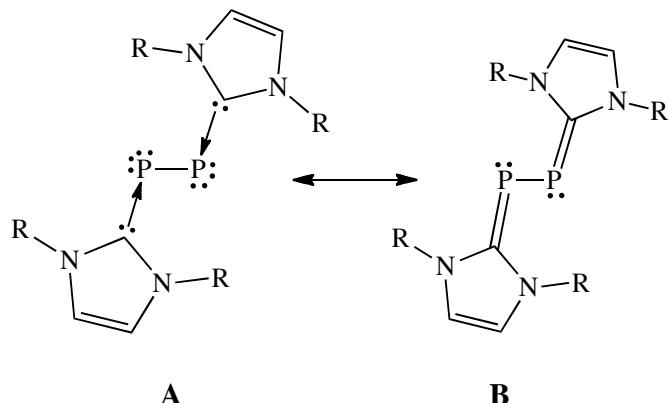


Figure 13. Canonical forms of carbene-stabilized P_2 .

1.6.8 N-Heterocyclic Carbene-Stabilized P_{12} Cluster

White phosphorus consists of four phosphorus atoms arranged in a tetrahedral fashion (Figure 14). This highly strained ring (P–P–P bond angle = 60°) is very reactive which ignites when exposed to air. Fragmentation of P_4 by transition metals^{157,158} is well known due to the presence of a coordinatively unsaturated metal center. In contrast, its reactivity towards main-group elements have only gained more attraction over the past five years.¹⁵⁹ As discussed in section 1.9.6, CAACs fragment P_4 into P_2 complexes. The reaction of NHCs with P_4 resulted in aggregation of P_4 into P_{12} cluster.¹⁶⁰

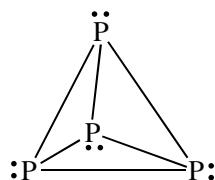
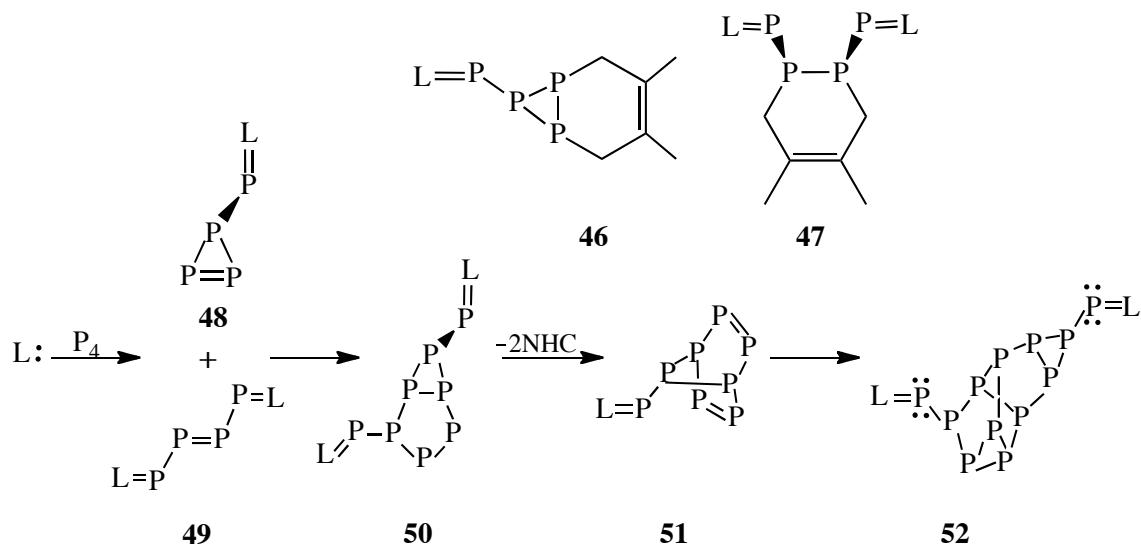


Figure 14. The Structure of P_4 , white phosphorus.

Heating a mixture of two equivalents of L: ($L = :C\{N(2,6-iPr_2C_6H_3)CH_2\}_2$) and P_4 to 70 °C, afforded a NHC-stabilized P_{12} cluster **52** in 81% yield. The X-ray structural analyses of **52** revealed three five-membered rings, two three-membered rings, and a six-membered ring. A combination of trapping experiments and DFT calculations were used to elucidate the formation of **52** (Scheme 20). Addition of L: to 0.5 equivalents of P_4 in the presence of 2,3-dimethyl butadiene afforded **46** and **47**, which were attributed to the [4 + 2] cycloaddition products of 2,3-dimethyl butadiene. Consequently, compounds **47** and **49** were identified as reaction intermediates. Moreover, the room temperature reaction monitored by ^{31}P NMR shows two sets of signals, similar to that in CAAC-stabilized P_2 (**45**), indicating the formation of **48**. However, these signals deteriorate overtime as the reaction undergoes further chemical transformation. Computations on these intermediates using the parent NHC suggested an exothermic cycloaddition to form **50**, which rearranges to **51** with loss of two NHCs. Finally **51** reacts with **48** to afford carbene-stabilized P_{12} cluster **52**.



Scheme 20. Proposed reaction pathway for the formation of NHC-stabilized P_{12} **52**.

The P–P bond lengths (2.176 – 2.233 Å) are comparable to those in **43** (2.205 Å), **44** (2.189 Å), and **45** (2.184 Å). Furthermore, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum displays two doublets at 189 ppm and 191 ppm indicating the presence of two P=C fragments. The two distinct reactivity products of P_4 with CAACs and NHCs is ascribed to the more electrophilic property of CAACs which strengthen the P=C bond, while NHCs are better leaving groups which favor the formation of a cluster.¹⁵⁶

1.7 Conclusion

The electronic and steric properties of carbenes have made them versatile tools in stabilizing highly reactive main group molecules. In particular, the utilization of NHCs to stabilize diatomic allotropes of the main group elements (B_2 , Si_2 , Ge_2 , Sn_2 , P_2 , As_2) demonstrates the unique stabilizing abilities of these ligands. Notably, the degree of steric bulk of the ligand and relative number of moles of reactants, coupled with the choice of reducing agent, solvent, and temperature can dramatically alter the chemistry of the resulting products. Therefore, the appropriate combination of reaction conditions is critical in the isolation of the products.

CHAPTER 2

RESULTS AND DISCUSSIONS

Our laboratory is interested in the utilization of sterically demanding ligands to stabilize low-oxidation state main group molecules containing element-element bonds. While this chemistry has been largely explored using formally anionic *m*-terphenyl ligands,⁴⁵⁻⁴⁷ the utilization of neutral carbene ligands have only recently emerged.^{47,77-79,161} Beginning with the first neutral diborene⁹⁵ in formal oxidation state of +1, a series of neutral diatomic molecules (disilicon,⁶³ diphosphorus,⁶⁴ and diarsenic⁶⁵) in the formal oxidation-state of zero have been isolated by our laboratory. These molecules have long been known to exist as highly reactive intermediates. For instance, the carbene-stabilized diatomic silicon molecule, **35** (section 1.6.5), consists of a Si=Si double bond and a lone pair of electrons on each silicon atom. These two features render the molecule to be highly reactive. Therefore, the preparation of soluble allotropes of these molecules provides a convenient way to conduct reactivity studies in their elemental form. Accordingly, our group continues to investigate different synthetic methods to synthesize these base-stabilized molecules and explore their various derivatives.

2.1 Carbene-Stabilized Diarsenic

While nitrogen exists exclusively as a diatomic molecule, phosphorus and arsenic, as heavier Group 15 congeners, exhibit diverse allotropy. For instance, P_4 and As_4 can pyrolyze to afford P_2 and As_2 , respectively. However, these products are only persistent at high temperatures.¹⁶² The bond dissociation energy decreases dramatically upon descending Group 15 ($N_2 = 226 \text{ kcal mol}^{-1}$, $P_2 = 116 \text{ kcal mol}^{-1}$,¹⁶³ and $As_2 = 83 \text{ kcal mol}^{-1}$),¹⁶⁴ which indicates the diminished importance of the $p\pi$ bonding with increasing atomic number. While N_2 usually¹⁶⁵ exhibits bonding mode **A** (triply bonded dipnictogen), P_2 and As_2 complexes can adopt either bonding mode **A** or bonding mode **B** (singly bonded dipnictogen) (Figure 15). The E_2 cores of P_2 and As_2 are known to serve as four-, six-, or eight-electron donor ligands in transition-metal (M)-carbonyl complexes (**C–G**).^{162,166,167} While compounds of type **C–F** adopt bonding mode **A**, compounds of type **G** exhibit bonding mode **B**. Herein, we demonstrate that As_2 compounds of type **B** can not only serve as electron-pair donors, but also serve as electron pair acceptors.

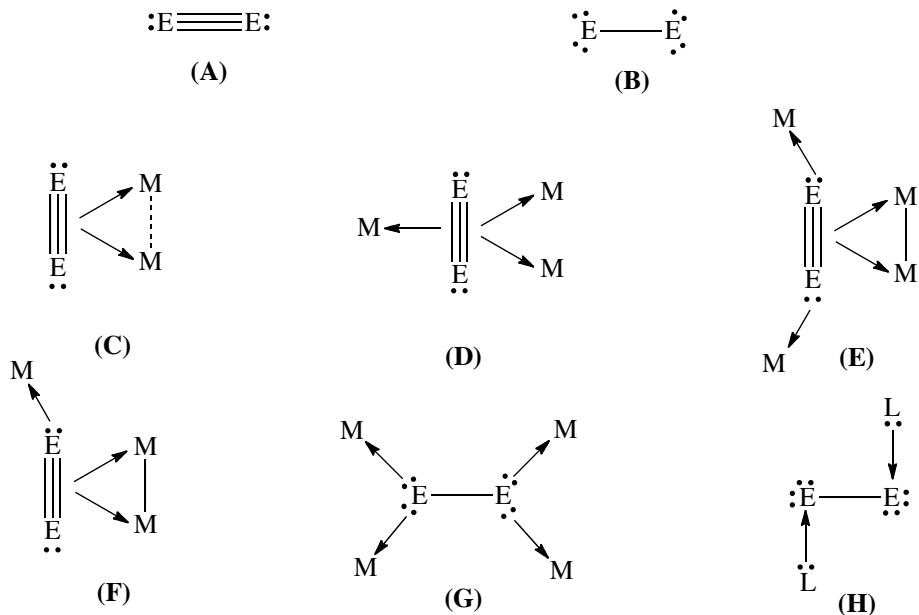
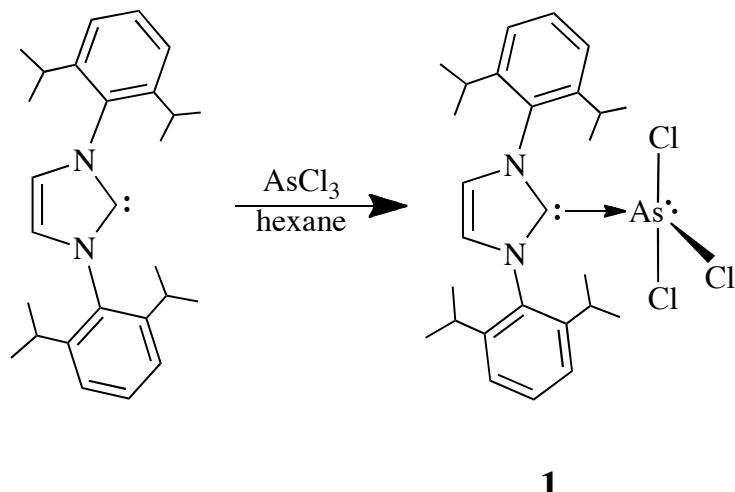


Figure 15. Various bonding modes for Diphosphorus and Diasrenic ($E = P$ or As).

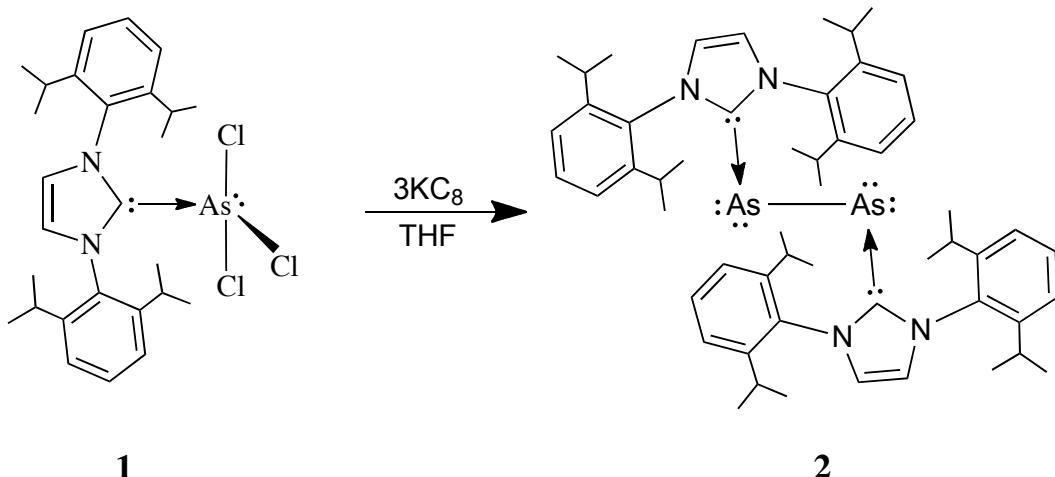
The previous reports of carbene-stabilized third row elements (Si_2 ,⁶³ P_1 ,¹⁵⁶ P_2 ,^{64,156} P_4 ,¹⁶⁸ and P_{12} ¹⁶⁰) inspired us to investigate the ability of NHCs to stabilize diatomic molecules residing in the fourth period or higher of the Periodic Table. Indeed, the synthesis of $\text{L}^1\text{:AsCl}_3$ **1** ($\text{L}^1\text{:} = \text{:C}\{\text{N}(2,6-\text{iPr}_2\text{C}_6\text{H}_3)\text{CH}\}_2$) followed by reduction using potassium graphite (KC_8) afforded the target compound $\text{L}^1\text{:As-As:L}^1$ **2** in 19.2% yield. It is worthy to note that the yield of As_2 is significantly lower than its phosphorus congener, P_2 (56.6%), which denotes the increased synthetic challenge of isolating carbene-stabilized dipnictidene complexes upon descending the group.

2.1.1 Synthesis and Molecular Structures of (1) and (2)

Immediately upon addition of AsCl_3 to $\text{L}^1\text{:}$ (Scheme 21), a white slurry was formed. The solvent was removed in vacuo and compound **1** was isolated as colorless crystals from a THF/toluene mixed solvent. The KC_8 reduction of **1** in THF resulted in a deep red solution (Scheme 22). The solvent was removed in vacuo and red crystals of $\text{L}^1\text{:As-As:L}^1$ **2** were obtained from a concentrated hexane solution.



Scheme 21. Synthesis of **1**.



Scheme 22. Synthesis of **2**.

The crystal structure of **1** reveals the presence of a four-coordinate arsenic atom with a truncated trigonal bipyramidal “see-saw” geometry (Figure 17). The equatorial positions are occupied by C(1) and Cl(1) atoms, while the remaining chlorides, Cl(2) and Cl(3), occupy the axial positions (Figure 16a). These structural features are similar to those in AsCl_4^- and $\text{L}^2:\text{AsCl}_3$ ($\text{L}^2: = \text{SC}\{\text{N}(\text{CH}_3)\text{CH}\}_2$) **3**.¹⁶⁹ On the contrary, the Lewis base ligand, L^3 , in $\text{L}^3:\text{AsCl}_3$ ($\text{L}^3: = :\text{N}(\text{CH}_3)_3$) **4** resides in an axial position (Figure 16b).¹⁷⁰ This structural variation may be attributed to the high electronegativity and the small size of the nitrogen in **4**.¹⁶⁹ The simplified model computed for $\text{L}^4:\text{AsCl}_3$ ($\text{L}^4: = \text{C}\{\text{N}(\text{H})\text{CH}\}_2$) **1-H** support the preference of the parent $\text{L}^4:$ ligand for the equatorial over the axial position as in **1**.

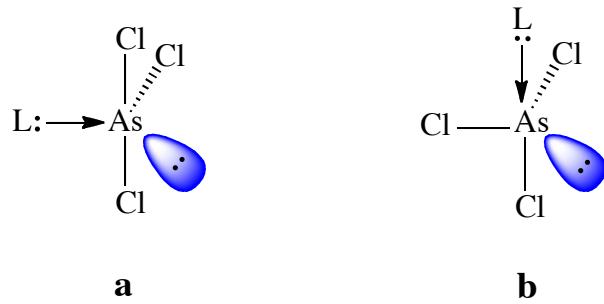


Figure 16. Examples of L: occupying equatorial (a) and axial positions (b) in L:AsCl₃ complexes.

The axial Cl(2)–As(1)–Cl(3) bond angle in **1** [178.65(13) $^{\circ}$] is the same as the N–As–Cl bond angle in **4** [178.7 $^{\circ}$], but larger than the Cl(2)–As(1)–Cl(3) of **3** [171.8 $^{\circ}$]. This difference maybe ascribed to the weak axial chlorine bridging interaction between the two neighboring molecules of **3** in the solid state.¹⁶⁹

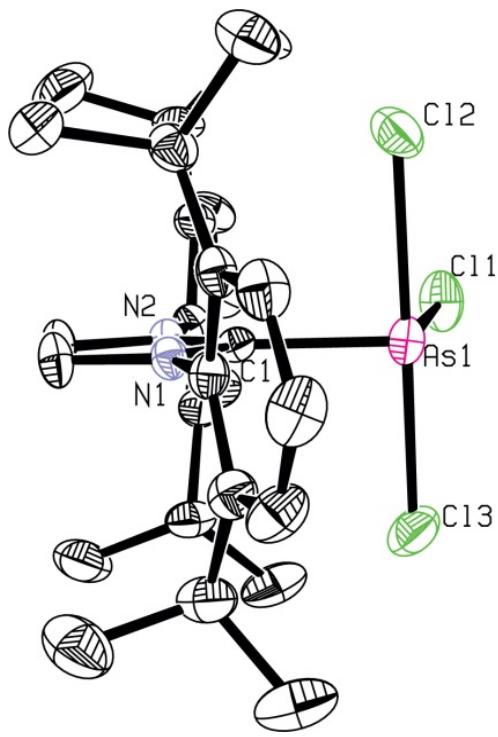


Figure 17. Molecular structure of **1**.

Table 1. Selected bond lengths [\AA] and angles [$^\circ$] of **1**.

Atoms	Distance	Atoms	Angle
As(1)–C(1)	2.018(3)	C(1)–As(1)–Cl(1)	99.92(10)
As(1)–Cl(1)	2.171(1)	C(1)–As(1)–Cl(2)	89.09(13)
As(1)–Cl(2)	2.484(2)	C(1)–As(1)–Cl(3)	90.35(14)
As(1)–Cl(3)	2.359(2)	Cl(1)–As(1)–Cl(2)	88.23(10)
		Cl(1)–As(1)–Cl(3)	90.65(8)
		Cl(2)–As(1)–Cl(3)	178.65(13)

Compound **2** has C_i symmetry and a trans-bent conformation about the As–As bond [C(1)–As(1A)–As(1)–C(1A) torsion angle = 180° ; Figure 18], and is isostructural to its P₂ congener [L:P–P:L] (L: = L¹) **5**.⁶⁴ The As–As bond length in **2** [2.442(1) Å] is the same as the As–As single bond distance in As₄ (2.44 Å),¹⁷¹ and compares well with the sum of As–As single bond covalent radii (2.42 Å).¹⁷² The C(1)–As(1)–As(1A) bond angle [101.11(5) $^\circ$] is about 2° less than the C(1)–P(1)–P(1A) bond angle in **5** [103.19(6) $^\circ$]. In addition, the As–As bond distance in **2** is approximately 0.24 Å longer than the P–P bond distance in **5** [2.205(1) Å]. The As–C_{carbene} bond length in **2** [1.881(2) Å] is similar to the reported values for carbene-arsinidene adducts [1.899(3)–1.902(7) Å].¹⁷³ This distance in **2** is shorter than that in **1** (2.0183(3) Å) but longer than As=C double bonds in acyclic arsaalkenes [(1.816–1.827) Å] indicating the partial As=C double bond character in **2**.¹⁷³ The imidazole rings and the As–As bond in **2** are almost coplanar [N(2)–C(1)–As(1)–As(1A) torsion angle = 2.0 $^\circ$], which is similar to the N(2)–C(1)–P(1)–P(1A) torsion angle [2.3 $^\circ$] in **5**.

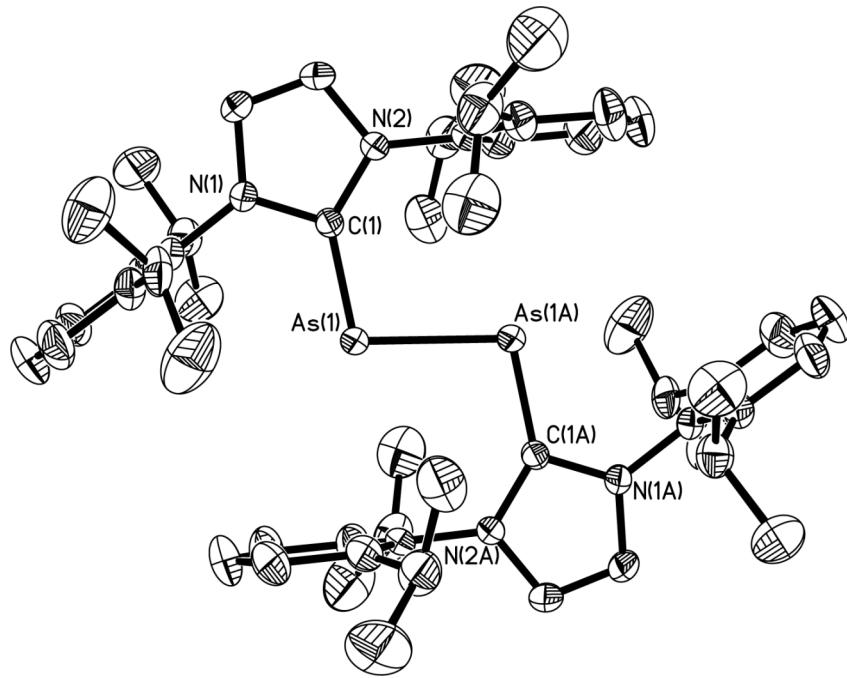


Figure 18. Molecular structure of **2**.

Table 2. Selected bond lengths [\AA] and angles [$^\circ$] of **2**.

Atoms	Distance	Atoms	Angle
As(1)–C(1)	1.881(2)	C(1)–As(1)–As(1A)	101.11(5)
As(1)–As(1A)	2.442(1)	N(1)–C(1)–As(1)	118.98(12)
		N(2)–C(1)–As(1)	137.63(13)

The DFT computations on the simplified $L^4\text{:As}-\text{As}:L^4$ ($L^4 = :\text{C}\{\text{N}(\text{H})\text{CH}\}_2$) model **2-H** prefers a gauche conformation in C_2 symmetry [torsion angle = (93.9°)], over the trans-bent geometry in **2** (Figure 19). A similar discrepancy has also been observed in **5**, which may be attributed to the considerable steric repulsion of the ligands in **2**. The computed As–As and As–C_{NHC} bond distances of **2-H** in C_2 symmetry are 2.464 Å and 1.928 Å respectively. In addition, the computed C–As–As angle is 95.4°. These parameters compare well with the experimental values for **2**.

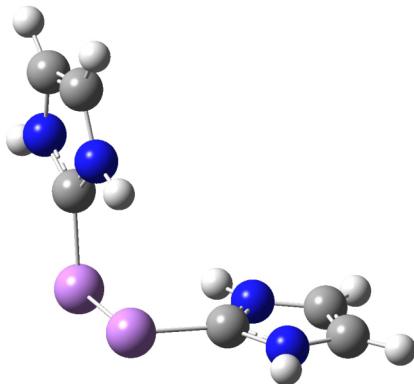


Figure 19. Optimized geometry of **2-H** model in C_2 symmetry.

The localized molecular orbitals (LMOs) of **2-H** optimized in C_i symmetry were computed using the X-ray coordinates of **2**. The LMOs and natural bond orbital (NBO) analysis further elucidate the bonding in **2**. LMO **a** (Figure 20a) shows the As–As σ -bond (Wiberg Bond Index (WBI) = 1.0009), which has predominately 4p character (8.9% s, 90.7% p, 0.4% d). The As–C_{NHC} σ -bond (WBI = 1.341) has a partial double-bond character: the As–C σ -bond formed by donation of a lone pair of electrons from the carbene to As is depicted in LMO **b** (Figure 20b), whereas the p π back-donation of the As lone-pair orbital with pure p character (0.0% s, 99.8% p, 0.2% d) to the empty p-orbital of the carbene ligand is depicted in LMO **c** (Figure 20c). While the As–C σ -bond polarization is 67.8% carbon and 32.2% (As has 15.4% s, 84.3% p, and 0.3% d

character), the $p\pi$ back-donation displayed in LMO **c** has 66.3% arsenic and 33.7% carbon polarization. LMO **d** (Figure 20d) depicts the As lone-pair orbital, which has 76.6% s, 23.3 % p, and 0.0% d character. In conclusion, compound **2** demonstrates the ability of NHC ligands to stabilize the diatomic As_2 molecule in the zero-oxidation-state.

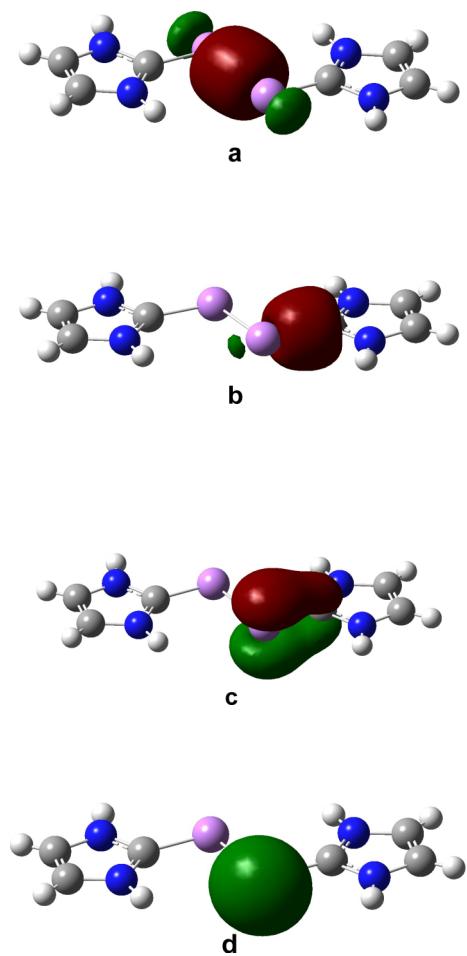


Figure 20. LMOs of **2-H** with C_i symmetry. a) As–As σ -bonding orbital; b) As–C σ -bonding orbital; c) lone-pair orbital (mainly p character) with $p\pi$ back-donation to the empty p of C_{NHC} ; d) lone-pair orbital (mainly s character).

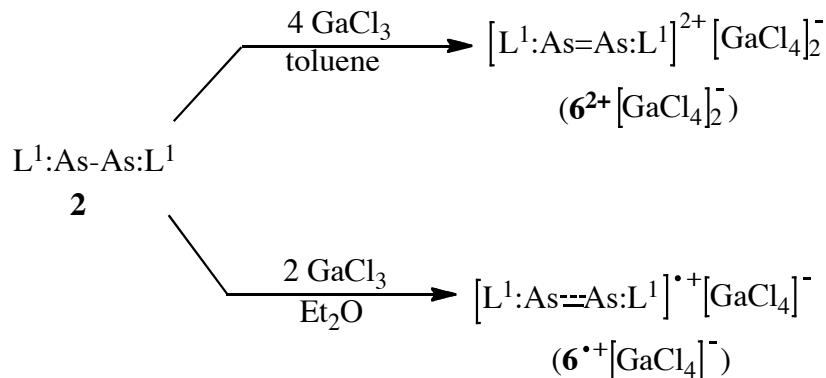
2.2 Oxidation of Carbene-Stabilized Diarsenic

Our laboratory is also actively pursuing reactivity studies of carbene-stabilized diatomic molecules. Indeed, our reports of the first “push–pull”-stabilized derivative of the parent silylene ($:SiH_2$) (Section 2.3), and the bidentate complexation of BH_2^+ to $L^1:P^-P:L^1(L^1:C\{N(2,6-iPr_2C_6H_3)CH\}_2)$ ¹⁷⁴ demonstrate the novel reactivity of these diatomic species. The electron-rich NHC-stabilized As_2 molecule, **2**, prompted us to investigate its reactivity toward Lewis acids. Consequently, we examined the room temperature reactivity of **2** with group 13 halides, ECl_3 ($E = Al, Ga, In$). Compounds $[L^1:As=As:L^1]^{+}[GaCl_4]^-$ (**6**⁺ $[GaCl_4]^-$), a NHC-stabilized monocationic diarsenic radical cation, and $[L^1:As=As:L^1]^{2+}[GaCl_4]^-_2$ (**6**²⁺ $[GaCl_4^-]_2$), a NHC-stabilized diarsene dication were isolated upon one- and two-electron oxidation of $L^1:As-As:L^1$ (**2**) by $GaCl_3$. Notably, compound **6**⁺ is the first arsenic radical to be structurally characterized.

It is pertinent to note that among the heavier group 15 elements, persistent¹⁷⁵ and stable¹⁷⁵ radicals have only been experimentally realized for phosphorus.¹⁷⁶⁻¹⁸¹ The one- and two-electron oxidization of carbene-stabilized P_2 , using $Ph_3C^+B(C_6F_5)_4$ and ferrocenium triflate respectively, has been recently reported by Bertrand.¹⁷⁶ On the contrary, the radical chemistry of arsenic, antimony, and bismuth have been largely unexplored.¹⁷⁵ To date, such species have only been studied experimentally by gas-phase electron diffraction¹⁸² and EPR spectroscopy.^{177,183} Although gallium halides are reportedly poor oxidizing reagents,¹⁸⁴ the oxidation of NHC-stabilized As_2 species, **2**, by $GaCl_3$, is reminiscent of the recently reported CAAC-stabilized boronylium complex ($H-B^+$), which was prepared upon one-electron oxidation of the corresponding parent borylene using $GaCl_3$.¹¹⁰

2.2.1 Synthesis and Molecular Structure of $\mathbf{6}^{\bullet+}[GaCl_4]^-$ and $\mathbf{6}^{2+}[GaCl_4^-]_2$

The reaction of **2** with two equivalents of $GaCl_3$ in ether afforded the green monocationic diarsenic radical complex $\mathbf{6}^{\bullet+}[GaCl_4]^-$ in 29.1% yield (Scheme 23). Notably, the addition of four equivalents of $GaCl_3$ to **2** resulted in orange dicationic diarsene complex $\mathbf{6}^{2+}[GaCl_4^-]_2$ in quantitative yield. Likewise, the addition of four equivalents of $AlCl_3$ or $InCl_3$ to **2** afforded the corresponding diarsene dications $\mathbf{6}^{2+}[ECl_4^-]_2$ ($E = Al, In$). Notably, the stability of $[L^1:As=As:L^1]^{2+}$ fragment may be affected by the counteranions $[ECl_4]^-$ ($E = Al, Ga, In$) in polar solvents. While the orange compound $\mathbf{6}^{2+}[ECl_4^-]_2$ ($E = Al, Ga$) remained orange upon addition of acetonitrile, the indium analog, $\mathbf{6}^{2+}[InCl_4^-]_2$, gradually decomposed with the color changing to green. Compound $\mathbf{6}^{\bullet+}[GaCl_4]^-$ was isolated as green crystals and characterized by EPR spectroscopy, whereas $\mathbf{6}^{2+}[GaCl_4^-]_2$ was isolated as orange crystals and characterized by NMR spectroscopy. In addition, both compounds were characterized by and single crystal X-ray crystallographic studies.



Scheme 23. Synthesis of $\mathbf{6}^{\bullet+}[GaCl_4]^-$ and $\mathbf{6}^{2+}[GaCl_4^-]_2$.

The X-ray data of $\mathbf{6}^{\bullet+}$ revealed that the As_2 core is disordered (only one set of disordered structural data is shown in Figure 21. The average As–As bond length in $\mathbf{6}^{\bullet+}$ (2.32 Å) lies between the As–As single bond in **2** (2.442(1) Å) and the As=As double

bond length in RAs=AsR' ($2.224(2)$ Å) [$R = 2,4,6$ -*t*Bu₃C₆H₂; R' = CH(SiMe₃)₂].³⁹ The average As–C bond distance in **6**^{•+} (1.92–1.95 Å) is slightly longer than those in **2** (1.881(2) Å). Model computations on **6-H**^{•+} ($L: = :C(NHCH)_2$; optimized in C₂ symmetry) showed an As–As bond distance of 2.388 Å, is about 0.06 Å longer than that in **6**^{•+}. The localized molecular orbitals (LMOs) of **6-H**^{•+} depicted on Figure 22 shows one As–As σ bonding orbital (a), one lone-pair orbital on each As atom (only one lone-pair shown) (b), one As–As π bonding orbital (c), and one As–As π^* singly occupied molecular orbital (d), which is in agreement with As–As Wiberg bond index (WBI) of 1.218. Natural bond orbital (NBO) analysis of **6-H**^{•+} showed a positive charge of +0.18 on each As atom, which is comparable to the positive charge of +0.16 on the P₂ unit in NHC-stabilized P₂^{•+} radical (**5**^{•+}).¹⁷⁶ Like **5**^{•+}, the spin density distribution of **6-H**^{•+} shows the localization of the unpaired electron at the As₂ core (0.41 at each As atom), which is in accordance with the SOMO shown in Figure 22.

The EPR spectrum of **6**^{•+} at room temperature in fluorobenzene displays a quintet ($g \approx 2.05$) (Figure 23). However, the expected EPR spectrum is a septet ($2nI + 1 = 2(2)(3/2) + 1 = 7$; where n = number of arsenic atoms = 2; I = electronic spin of arsenic = 3/2). This discrepancy is due to the poorly resolved low- and high-field hyperfine components resulting from large hyperfine coupling with two equivalent ⁷⁵As ($I = 3/2$) nuclei ($A \approx 68$ MHz). The correlation time estimated from parallel NMR studies (10^{-5}), was used to obtain a well-simulated spectrum of the diarsenic radical involving two equivalent As atoms (simulation parameters are shown in Figure 23 caption). Therefore, the EPR data clearly supports the radical nature of **6**^{•+}.

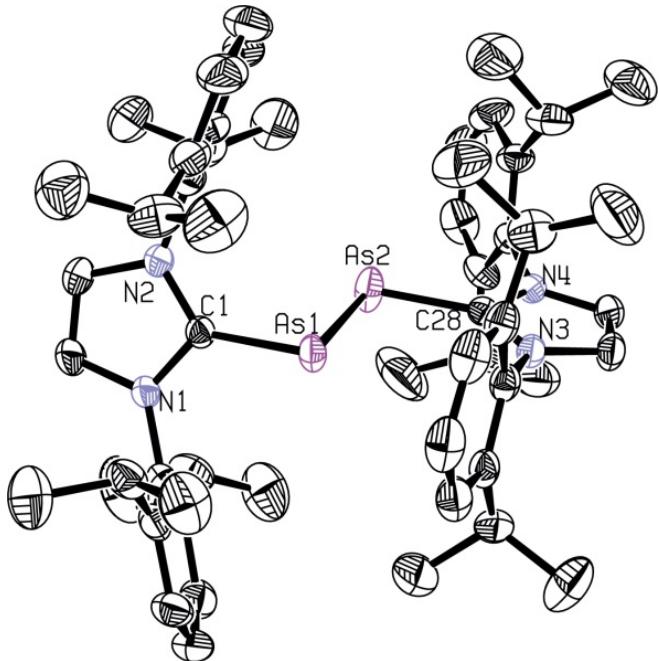


Figure 21. Molecular structure of $\mathbf{6}^{\bullet+}$.

Table 3. Selected bond lengths [\AA] and angles [$^\circ$] of $\mathbf{6}^{\bullet+}$.

Atoms	Distance	Atoms	Angle
As(1)-As(2)	2.332(3)	C(1)-As(1)-As(2)	92.10(14)
As(1)-C(1)	1.960(4)	C(28)-As(2)-As(1)	101.02(16)
As(2)-C(28)	1.938(5)	N(1)-C(1)-As(1)	123.9(3)
C(1)-N(1)	1.358(5)	N(2)-C(1)-As(1)	129.0(3)
C(1)-N(2)	1.346(5)	N(3)-C(28)-As(2)	135.3(3)
C(28)-N(3)	1.357(5)	N(4)-C(28)-As(2)	118.9(3)
C(28)-N(4)	1.359(5)		

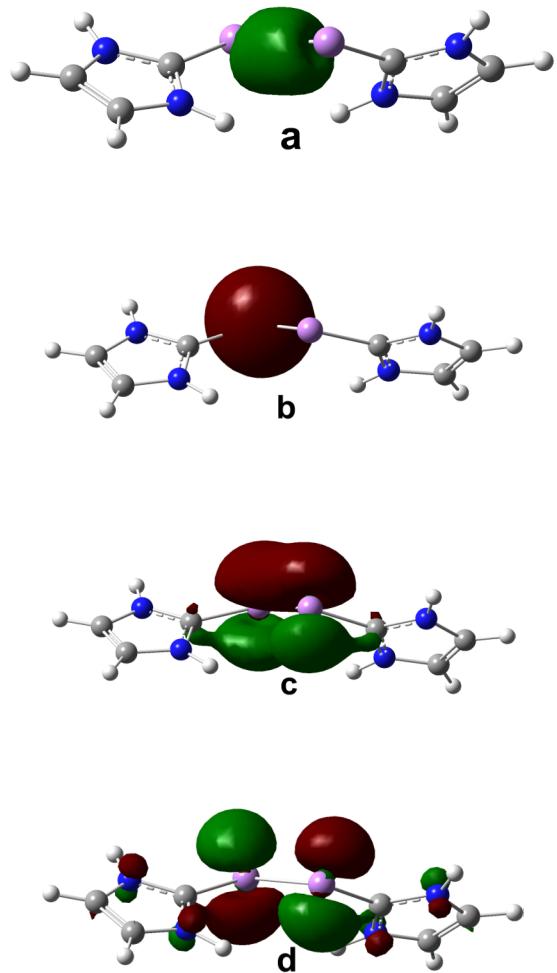


Figure 22. LMOs of **6** \cdot H^+ with C₂ symmetry. a) As–As σ -bonding orbital; b) one of the two As lone-pair orbital; c) As–As π bonding orbital; d) As–As π^* antibonding SOMO.

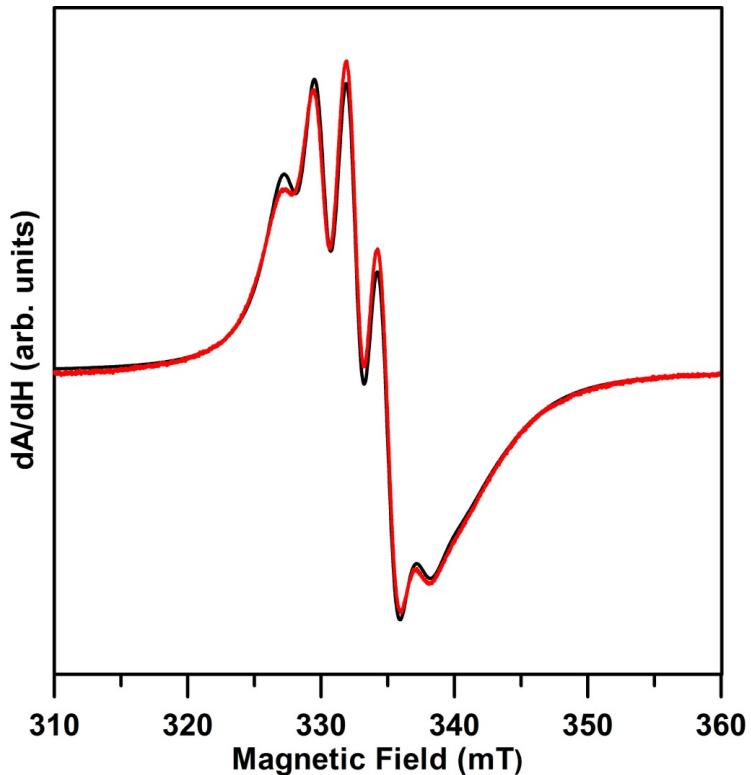


Figure 23. Room-temperature X-band EPR spectrum of $\mathbf{6}^+$ in fluorobenzene (red line) recorded at 9.59 GHz with a modulation amplitude of 1 mT and a microwave power of 80 mW. The almost perfectly superposed simulated spectrum (black line) was generated with EasySpin software package using a correlation time of 10^{-5} s, with $g_{x,y,z} = 2.0458$, 2.0457, 2.0452, and two identical ^{75}As ($I = 3/2$) nuclei with $A_{x,y,z} = 67.1$, 68.0, 67.8 MHz.

Similar to **2**, the X-ray structural analysis of **6**²⁺ (Figure 24) shows C_i symmetry and a trans-bent geometry about the As–As bond (C(1)–As(1)–As(1A)–C(1A) torsion angle = 180°). The C(1)–As(1)–As(1A) bond angle of **6**²⁺ (100.1(7) Å) is similar to that in **2** (101.11(5) Å). The As=As bond distance in **6**²⁺ (2.2803(5) Å) is slightly shorter than that in **6**^{•+} (2.32 Å av) and about 0.16 Å shorter than that in **2** (2.442 (1) Å). However, the As=As double bond in **6**²⁺ is longer than the As=As double bond in RAs=AsR' (2.224(2) Å)³⁹ by 0.06 Å. The As–C bond lengths in **6**²⁺ (1.9772(2) Å) is 0.1 Å longer than that in **2** (1.881(2) Å) and marginally shorter than those in **6**^{•+} (1.92–1.95 Å av). A similar trend have been observed in the P–P bond distances and P–C bond distances in NHC-stabilized P₂ (**5**) and its oxidized derivatives **5**^{•+} and **5**²⁺.¹⁷⁶ The simplified model **6-H**²⁺, where L: = :C(NHCH)₂, shows that the As=As and As–C bond lengths are comparable to those in **6**²⁺ (As=As = 2.2803(5) Å; As–C = 1.9772(2) Å). The LMOs depicted in Figure 25 show the presence of one As–As σ-bond (a), and one As–As π-bond (b) in **6-H**²⁺. The WBI of **6-H**²⁺ (1.78) supports the double bond character of As=As in **6**²⁺. Moreover, the +0.77 positive partial charge on **6**²⁺ is similar to the +0.73 partial charge on the **5**²⁺.¹⁷⁶

The increase in bond order with increased oxidation number might seem counterintuitive, however, the Molecular Orbital (MO) diagrams of **2**, **6**^{•+}, and **6**²⁺ (Figure 26) unambiguously support the assigned bond orders. The MO of **2** depicts the presence of one As–As σ-bond, one As–As π-bond, one lone pair of electron (mainly s character), and a second lone pair orbital (mainly p character) in the highest occupied molecular orbital (HOMO) (Figure 26a). The net bond order of 1.0 in **2** increases to 1.5 upon one-electron oxidation from the HOMO to give **6**^{•+} (Figure 26). The subsequent one-electron oxidation of **6**^{•+} results in a net bond order of 2.0 to give **6**²⁺ (Figure 26).

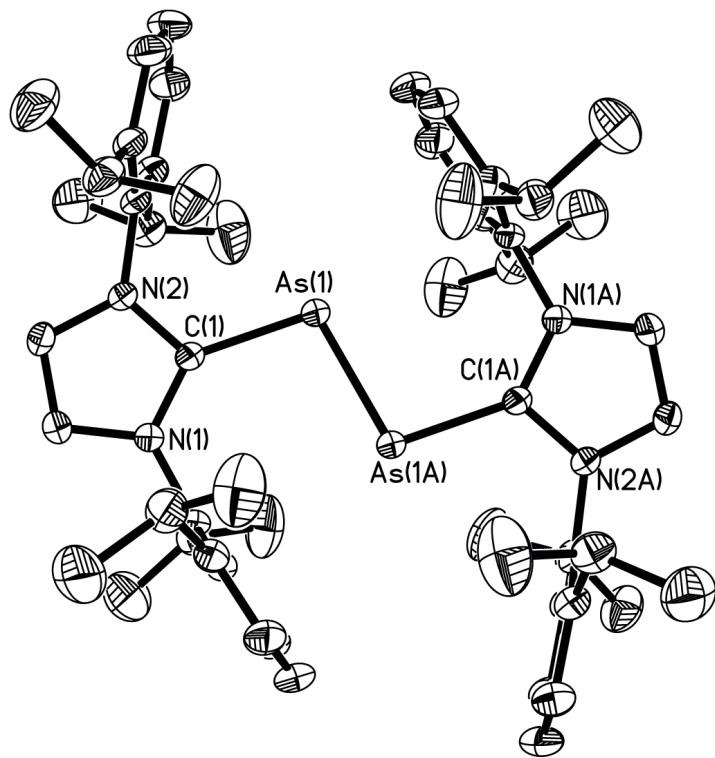


Figure 24. Molecular structure of $\mathbf{6}^{2+}$.

Table 4. Selected bond lengths [\AA] and angles [$^\circ$] of $\mathbf{6}^{2+}$.

Atoms	Distance	Atoms	Angle
As(1)–As(1A)	2.2803(5)	C(1)–As(1)–As(1A)	100.10(7)
As(1)–C(1)	1.977(2)	N(1)–C(1)–As(1)	135.61(17)
C(1)–N(1)	1.353(3)	N(2)–C(1)–As(1)	118.70(17)
C(1)–N(2)	1.351(3)		

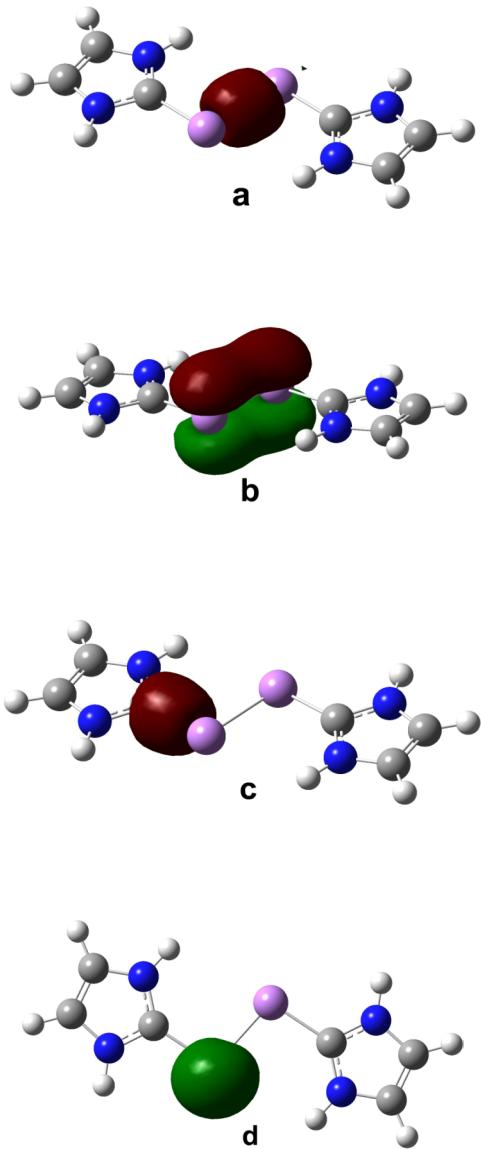


Figure 25. LMOs of **6** \cdot H_2^+ with C_i symmetry: a) As–As σ -bonding orbital; b) As–As π bonding orbital; c) one of the As–C σ -bonding orbitals; d) one of the As lone-pair orbitals.

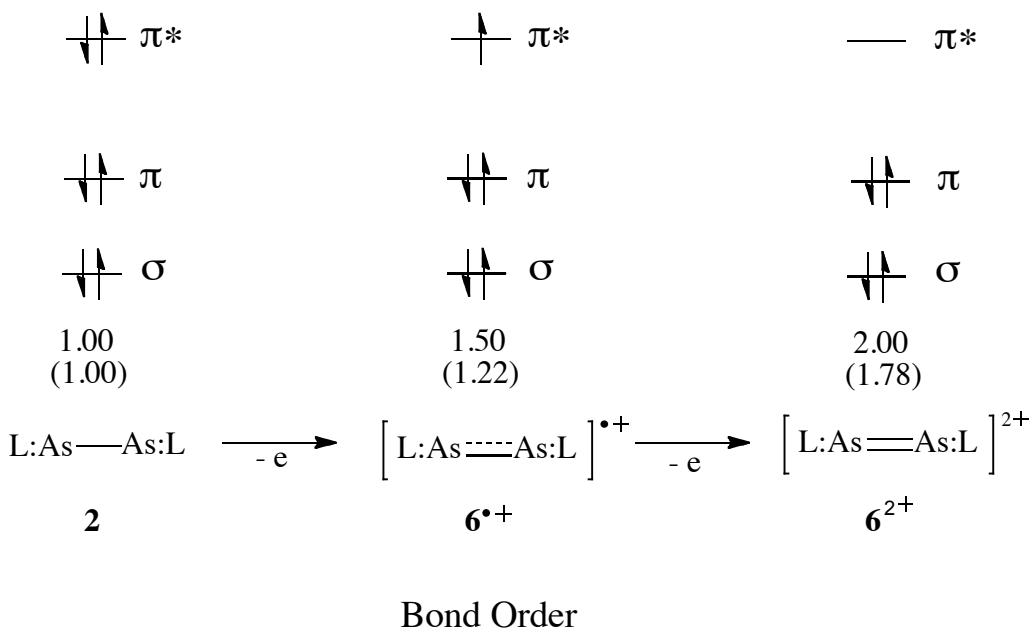


Figure 26. Molecular orbital diagrams of **2**, **6^{•+}**, and **6²⁺**.

Theoretical bond orders can be calculated by the equation: (electrons in bonding molecular orbitals – electrons in antibonding molecular orbitals)/2. Therefore, the bond orders 1.00, 1.50, and 2.00 are expected for **2**, **6^{•+}**, and **6²⁺** respectively (Figure 26). The computed bond orders 1.00, 1.22, and 1.78 (shown in parentheses in Figure 26) are in close agreement with the calculated values.

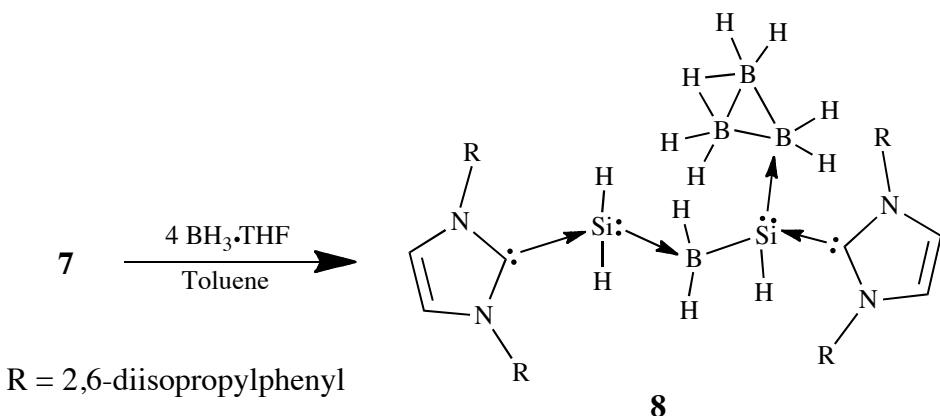
In conclusion, the NHC-stabilized diarsenic compound, undergoes one- and two-electron oxidization using two and four equivalents of GaCl_3 respectively. Notably, the carbene-stabilized diarsene dication, **6^{•+}**, is the first arsenic radical to be structurally characterized.

2.3 Cleavage of Carbene-Stabilized Disilicon

One of the most studied reactions in organic chemistry is the hydroboration of alkenes. However, hydroboration of disilenes have only been explored computationally.¹⁸⁵ Recently, Sekiguchi⁵¹ demonstrated the reactivity of disilyne, $\text{RSi}\equiv\text{SiR}$ ($\text{R} = \text{SiPr}^i[\text{CH}(\text{SiMe}_3)_2]_2$), with 9–BBN (9-borabicyclo[3.3.1]nonan-9-yl) and catecholborane gives boryl-substituted disilenes.^{186,187} Similarly, we have examined the hydroboration reaction to carbene-stabilized disilicon, $\text{L}^1:\text{Si}=\text{Si}:\text{L}^1$ **7** ($\text{L}^1: = :\text{C}\{\text{N}(2,6-\text{iPr}_2\text{C}_6\text{H}_3)\text{CH}\}_2$). Compound **7** has a unique electronic property compared to previously synthesized disilenes since it retains a lone pair of electrons on each silicon atom rather than use all the electrons for bonding. This property could potentially allow it to function as a Lewis base, which readily coordinates with Lewis acids. Therefore, we were prompted to explore its reactivity with $\text{BH}_3\cdot\text{THF}$. Instead of forming a typical Lewis acid – Lewis base adduct, pure crystals of **7** underwent cleavage of the Si=Si double bond to afford compound **8** in 71.7% yield. (Scheme 2.4).¹⁸⁸ Alternatively, the addition of $\text{BH}_3\cdot\text{THF}$ to a mixture of **7** and $\text{L}^1:$ (5:1; determined by ^1H NMR) afforded compound **9** in 28.2% yield along with **8** in 30.3% yield (Scheme 2.4). It is noteworthy that a similar reactivity study has been conducted on NHC-stabilized diphosphorus, $\text{L}^1:\text{P}=\text{P}:\text{L}^1$ (**5**). The addition of excess $\text{BH}_3\cdot\text{THF}$ to **5** surprisingly afforded the $\text{L}^1:\text{P}=\text{P}:\text{L}^1$ -complexed dihydroboronium salt wherein a lone pair from each phosphorus atom are used to chelate to one BH_2^+ cation.¹⁷⁴ Notably, a lone pair of electrons remained on each phosphorus atom even upon adding excess $\text{BH}_3\cdot\text{THF}$, which maybe attributed to the presence of sterically encumbered carbene ligands.

2.3.1 Synthesis and Molecular Structure of **8**

Compound **7** was prepared as previously described.⁶³ The addition of four equivalents of 1.0M $\text{BH}_3\text{-THF}$ to **7** in toluene was performed at room temperature (Scheme 24). Immediately upon addition, the color of the solution changed from dark red to brown-orange. After 16 h of stirring, all solvent was removed to give an oily residue. The product was isolated as colorless crystals from THF/hexane mixed solvent (1:4) and characterized by single crystal X-ray crystallography, ^1H NMR, ^{11}B NMR, and melting point determination.



Scheme 24. Synthesis of **8**.

The crystal structure of **8** (Figure 27) suggests a complex sequence of reactions involving the cleavage of the $\text{Si}=\text{Si}$ double bond and insertion of a BH_2 moiety, as well as boron-to-silicon transfer of hydrogen atoms. In addition, the aggregation of three BH_3 moieties into a neutral three-membered B_3H_7 ring with loss of two hydrogens was also observed. Notably, an electron pair from the $\text{Si}(1)$ atom is used to stabilize the B_3H_7 ring. Similar interaction with a B_3H_7 ring has been reported for amines,¹⁸⁹ phosphines,¹⁹⁰ and carbonyls.¹⁹¹ The most striking feature of **8** is the presence of “push–pull” stabilized parent silylene ($:\text{SiH}_2$) unit. Prior to our report, a method well-known for the preparation

of parent silylenes is photolysis of phenylsilane by ultraviolet light (193 nm),¹⁹² which are only stable in an argon matrix at $-190\text{ }^{\circ}\text{C}$.¹⁹³ At room temperature, insoluble products are formed due to the polymerization or disproportionation of the silylene moieties. Silylenes have also been observed as an intermediate during the chemical vapor deposition (CVD) of silicon film by pyrolysis of silane (SiH_4).¹⁹⁴ The “push-pull” NHC–transition metal carbonyl complexed GeH_2 and SnH_2 analogues have been recently isolated.^{195–197} Similarly, **8** is the first example of a “push–pull” stabilized parent silylene, which is stable at room temperature. Indeed, theoretical studies have suggested that the coordination of silylenes to a Lewis base decreases its electron deficiency, which in turn triggers the nucleophilic character of silylenes.¹⁹⁸ Like the R groups ($\text{R} = \text{BH}_3, \text{W}(\text{CO})_5$) in NHC-stabilized GeH_2 and SnH_2 complexes, the $\text{L}^1:\text{SiH}(\text{BH}_2)(\text{B}_3\text{H}_7)$ fragment in **8** serves as a Lewis acid.

The four-coordinate silicon atoms, Si(1) and Si(2), in **8** adopt a tetrahedral geometry and bear a formal oxidation state of +2 (Figure 27). The bond distances between the Si(1)–(C1) (1.944(4) Å) and Si(2)–(C28) (1.934(4) Å) in **8** are comparable to those reported for **7** (1.927(15) Å).⁶³ The average B(1)–Si(1) (1.980 Å) and B(1)–Si(2) (1.902 Å) bond lengths, are similar to the bond length in B(2)–Si(1) (1.965(7) Å). Theoretical studies also predict similar bond lengths for donor-acceptor interaction between silylenes and borane [$(\text{H}_3\text{N})(\text{SiH}_2)\rightarrow\text{BH}_3 = 1.973\text{ }\text{\AA}$; $(\text{NHC})(\text{SiH}_2)\rightarrow\text{BH}_3 = 1.999\text{ }\text{\AA}$].¹⁹⁸ The ^1H NMR displays a singlet resonance at -0.29 ppm, while the ^{11}B NMR displays a multiplet at -30 ppm, both of which were assigned to the B_3H_7 ring in **8**. In contrast to the ^1H NMR resonances in $\text{H}_3\text{N}:\text{B}_3\text{H}_7$ (1.62 ppm)¹⁸⁹ and $\text{L}:\text{B}_3\text{H}_7$ ($\text{L:} = \text{PH}_3, \text{CH}_3\text{PH}_2, (\text{CH}_3)_2\text{PH}, (\text{CH}_3)_3\text{P}$) (1.23 – 0.72 ppm)¹⁹⁰ are located downfield. The resonance of the silylene

coordinated B_3H_7 is shifted to a higher field (-0.29 ppm) which suggests the stronger electron-donating ability of silylene than phosphine or ammonia. Although the BH_2 proton resonances were not observed in the ^1H NMR,^{199,200} they were clearly seen as a triplet in the proton coupled ^{13}B NMR (-50.4 ppm). This position similar to that in $[\text{Tbt}(\text{Mes})\text{SiHBH}_2\text{CNAr}; \text{Tbt} = 2,4,6\text{-tris[bis(trimethylsilyl)methyl]phenyl}]$ (-43.0 ppm).²⁰⁰ The ^{29}Si atoms in **8** could not be observed due to the strong line-broadening caused by quadrupolar boron nuclei.²⁰¹ However, the ^1H NMR resonance of **8** displayed a SiH doublet at 2.90 ppm ($J = 7.0$ Hz)¹⁹⁹ and a SiH_2 triplet at 3.13 ppm ($J = 12.0$ Hz).

Density functional theory (DFT) computations at the B3LYP/DZP level were used to further probe the bonding nature of **8**. The computed bond distances for $\text{B}(1)\text{--Si}(1)$ (2.036 Å), and $\text{B}(1)\text{--Si}(2)$ (2.006 Å) are only marginally longer than the experimental bond distances (1.980 Å and 1.902 Å, respectively). In addition, the computed $\text{Si}(1)\text{--B}(1)\text{--Si}(2)$ bond angle of 104.7° compares well to the experimental value of 110.6° . The Wiberg bond indices 0.953 of $\text{B}(1)\text{--Si}(1)$, 0.999 of $\text{B}(1)\text{--Si}(2)$, and 0.869 of $\text{B}(2)\text{--Si}(1)$, support their single bond essence. Furthermore, the dative character of $\text{B}(1)\text{--Si}(2)$ and $\text{B}(2)\text{--Si}(1)$ in **8** is supported by the computed positive natural charges, $+0.95$ for $\text{Si}(1)$ and $+0.90$ for $\text{Si}(2)$, and the negative charges, -0.92 for $\text{B}(1)$ and -1.03 for the B_3H_7 ring.

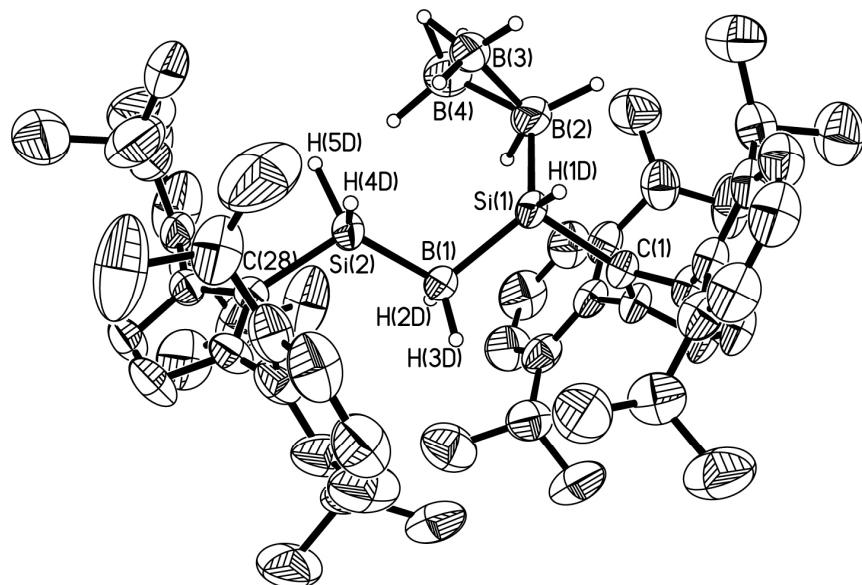


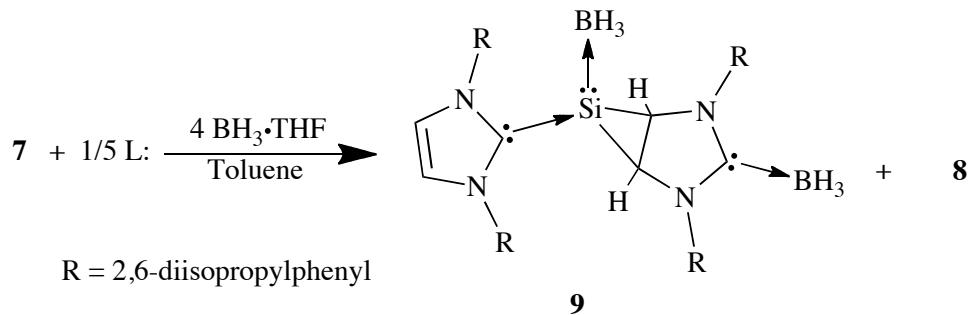
Figure 27. Molecular structure of **8**.

Table 5. Selected bond lengths [\AA] and angles [$^\circ$] of **8**.

Atoms	Distance	Atoms	Angle
Si(1)–C(1)	1.944(4)	C(1)–Si(1)–B(1)	107.2(2)
Si(2)–C(28)	1.934(4)	B(1)–Si(2)–C(28)	117.7(3)
B(1)–Si(1)	1.994(8)	Si(1)–B(1)–Si(2)	109.1(4)
B(1)–Si(2)	1.922(7)	B(2)–Si(1)–B(1)	122.2(3)
Si(2)–H(4D)	1.49(2)	B(2)–Si(1)–C(1)	107.7(2)
Si(2)–H(5D)	1.42(4)	B(2)–Si(1)–H(1D)	111.0(14)
B(1)–H(3D)	1.119(19)	H(2D)–B(1)–H(3D)	106(3)
B(1)–H(2D)	1.145(19)	H(4D)–Si(2)–H(5D)	101(3)
Si(1)–H(1D)	1.49(4)		
B(2)–Si(1)	1.965(7)		

2.3.2 Synthesis and Molecular Structure of **9**

Compound **7** was prepared as previously described.⁶³ However, instead of crystallizing the raw material, it was repeatedly washed with hexane until the ratio of **7** to L¹: reached 5:1 (determined by ¹H NMR). The addition of 1.0M BH₃·THF to a mixture of **7** and L¹: (BH₃·THF: **7** = 4:1) in toluene was carried out at room temperature (Scheme 25). As in the formation of **8**, the color of the solution immediately changed from dark red to brown-orange. In addition, a substantial amount of white precipitate was observed which was indicative of a second compound, which is insoluble in toluene. The solution was filtered and the precipitate was dried and redissolved in DME/THF/hexane. Compound **9** was isolated as colorless crystals. The solvent from the filtrate was removed in vaccuo, which gave an oily residue. The ¹H NMR spectrum of this raw material indicated the presence of **8** and **9**, which implied that **9** is partially soluble in toluene. Therefore the raw material was repeatedly rinsed with small amounts of toluene in order to separate **8** from **9** (confirmed by ¹H NMR). Compound **9** was characterized by single crystal X-ray crystallography, ¹H NMR, ¹¹B NMR, and melting point determination.



Scheme 25. Synthesis of **9**.

The X-ray structure of **9** (Figure 28) reveals a three-membered silylene ring. The silicon atom donates a lone pair of electrons to a BH₃ molecule (nucleophilic character)

while also accepting a lone pair of electrons from the carbene ligand (electrophilic character). This “push-pull” bonding character is similar to that observed in compound **8**. The remaining two valence electrons of silicon form single bonds with the C(2) and C(3) carbons on the L:BH₃ adduct. While five- and six-membered cyclosilylenes are well-known, three-membered cyclic silylene of the form C₂H₄Si: have only been studied by matrix-spectroscopic studies.²⁰² Although the mechanism is unclear, the formation of **9** may be ascribed to the cycloaddition of a highly reactive Si(0) center of an L:Si(BH₃) intermediate to the C=C double bond of an imidazole ring in a L:BH₃ adduct. Indeed, such reactions of π -conjugated systems with Si(0) atoms have been observed in matrix isolation spectroscopy.²⁰²⁻²⁰⁴ It is pertinent to note that the presence of free NHC ligands in the reaction mixture seems to be essential since it serves as a “trapping agent” for the “push-pull” stabilized Si(0) atom.

The central silicon atom is four-coordinate and adopts a distorted tetrahedral geometry (Figure 28). The three-membered cyclic silylene ring in **9** has a C(2)–C(3) bond distance of 1.530(4) Å, which is longer than a C=C double bond in unsaturated NHCs (1.33 Å)⁸⁸ and corresponds to a C–C single bond in saturated NHCs (1.504 Å).⁸⁸ The Si(1)–C(28) dative bond (1.938(3) Å) is slightly longer than in Si(1)–C(2), and Si(1)–C(3) bonds distances (1.903(3) Å and 1.888(3) Å respectively). They are also comparable to the Si(1)–C(1), and Si(2)–C(28) bond distances (1.944(4) Å and 1.934(4) Å respectively) in **7**.

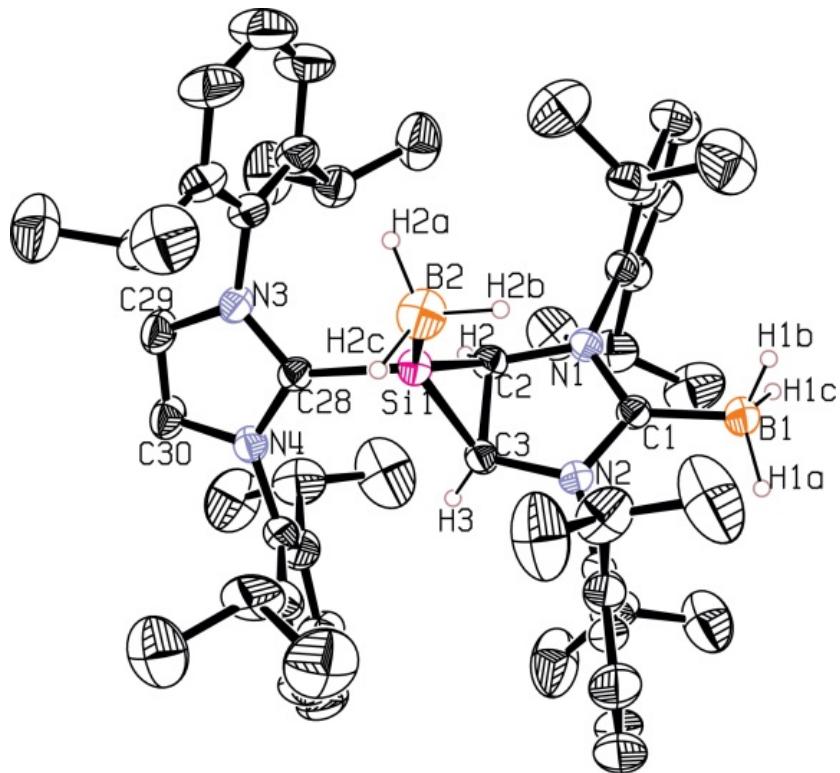


Figure 28. Molecular structure of **9**.

Table 6. Selected bond lengths [\AA] and angles [$^\circ$] of **9**.

Atoms	Distance	Atoms	Angle
Si(1)–B(2)	1.996(4)	C(2)–Si(1)–B(2)	134.88(17)
Si(1)–C(28)	1.938(3)	C(3)–Si(1)–B(2)	133.06(18)
Si(1)–C(2)	1.903(3)	C(28)–Si(1)–B(2)	116.25(17)
Si(1)–C(3)	1.888(3)	C(2)–Si(1)–C(28)	102.27(13)
C(2)–C(3)	1.530(4)	C(3)–Si(1)–C(28)	104.04(13)
C(1)–B(1)	1.593(5)	C(3)–Si(1)–C(2)	47.62(12)
		C(3)–C(2)–Si(1)	65.68(16)
		C(2)–C(3)–Si(1)	66.70(16)

The proton-coupled ^{11}B NMR spectrum of **9** gave a quartet resonance (-35 ppm, $^1J = 83$ Hz) of the BH_3 at the C(1) carbene center, which compares well with that reported $\text{L}^1:\text{BH}_3$ (-35.4 ppm; $^1J = 83$ Hz).⁹⁵ Furthermore, the broad doublet resonance of the BH_3 coordinated to the silicon atom (-47.0 ppm) is similar to that in potassium tris(trimethylsilyl)silylboranate²⁰¹ (-43.4 ppm, $^1J = 84$ Hz). Like **7**, the ^{29}Si resonance of the central silicon atom could not be observed.²⁰¹

In summary, the reactivity of NHC-stabilized disilicon, **7**, with BH_3 afforded compound **8**, which contains the first parent silylene ($:\text{SiH}_2$) moiety that is stable under ambient conditions. Like the parent germylene ($:\text{GeH}_2$) and stannylene ($:\text{SnH}_2$) monomers, the “push-pull” stabilization strategy involving NHCs, has proven to be effective in stabilizing the silicon congener. In addition, the presence of free carbene in the reaction mixture has served as a “trapping-agent” for stabilizing the first three-membered silylene ring in compound **9**. Like **8**, the isolation of **9** also involves a “push-pull” bonding character, wherein the electron-donor ligand is also a carbene ligand.

CHAPTER 3

CONCLUSIONS

3.1. Concluding remarks

The goal of my research was to utilize sterically demanding N-heterocyclic carbenes as stabilizing ligands for the isolation of diatomic allotropes of the main group elements. In addition, my research also included reactivity studies of these base stabilized molecules. I found this area of research to be challenging, yet rewarding as it has led to the isolation of various novel molecules. Not only does the synthesis of these molecules require appropriate reaction conditions, but also the determination of the suitable crystallization conditions. However, the stabilizing capability of NHCs is now well-recognized and many novel molecules can be potentially isolated.

The NHC ligand that was frequently used in my research is L¹: (L¹: = :C{N(2,6-^tPr₂C₆H₃)CH}₂). This ligand was chosen as it has previously demonstrated its ability to stabilize novel homonuclear diatomic molecules. In particular, the isolation of the first neutral diborene (L¹:(H)B=B(H):L¹), and the soluble diatomic allotropes of silicon and phosphorus by our laboratory were encouraging. Using a similar synthetic strategy, I sought to evaluate the ability of L¹: to stabilize heavier main-group molecules residing in the fourth period of the periodic table. Indeed, the potassium graphite reduction of L¹:AsCl₃ afforded L¹:As–As:L¹ (**2**). Compound **2** exhibits similar structural features to its phosphorus congener. However, the low yields (56.6% for P₂ and 19.2% for As₂ as

determined by NMR) demonstrated the increased synthetic challenge in isolating the diatomic allotropes of the heavier main group elements.

We also examined the reactivity of **2** toward group 13 halides. Upon addition of two equivalents of GaCl_3 , **2** underwent one-electron oxidation to give a monocationic diarsenic radical complex $[\text{L}^1:\text{As}=\text{As:L}]^{+}[\text{GaCl}_4]^{-}$ (**6** $^{+}[\text{GaCl}_4]^{-}$). Conversely, the addition of four equivalents of GaCl_3 to **2** resulted in two-electron oxidation **2** to give a dicationic diarsene complex $[\text{L}^1:\text{As}=\text{As:L}]^{2+}[\text{GaCl}_4]^{-}_2$ (**6** $^{2+}[\text{GaCl}_4^{-}]_2$). While AlCl_3 and InCl_3 were also capable of forming the two-electron oxidized products, **6** $^{2+}[\text{ECl}_4^{-}]_2$ ($\text{E} = \text{Al}$ or In), the stability of the dicationic fragment seemed to be affected by the counteranion. Specifically, the orange color of **6** $^{2+}[\text{ECl}_4^{-}]_2$ ($\text{E} = \text{Ga}$ or Al) was retained upon addition of acetonitrile, whereas the color **6** $^{2+}[\text{InCl}_4^{-}]_2$ in acetonitrile gradually changed to green. It is pertinent to note that an increase in the net bond order (computed bond orders: 1.0 in **2**, 1.22 in **6** $^{+}$, and 1.78 in **6** $^{2+}$) was found with subsequent one-electron oxidation of **2**. This is due to the successive one electron loss from the π^* molecular orbital. These results demonstrate the unusual oxidizing capability of GaCl_3 . Notably, **6** $^{+}$ is the first arsenic radical to be structurally characterized in the solid state.

The reactivity of $\text{L}^1:\text{Si}=\text{Si}:\text{L}^1$ (**7**) toward BH_3 was also evaluated. Surprisingly, cleavage of the Si=Si double bond occurred to afford two unique compounds: the first compound containing a “push–pull” stabilized parent silylene (**8**), and a second compound containing a three-membered cyclic silylene (**9**). While **8** was obtained from the reaction of pure crystals of **7** with BH_3 , the presence of free carbene $\text{L}^1:$ ($7:\text{L}^1: = 5:1$) in the reaction mixture induced the formation of **9**. Therefore, $\text{L}:$ can be considered a “trapping agent” for the “push–pull” stabilized Si(0) atom in **9**.

To conclude, my research efforts have contributed to demonstrating the utility of N-heterocyclic carbenes in stabilizing highly reactive main-group molecules. Since the isolation of main-group diatomic allotropes has only recently emerged, a number of novel derivatives can be expected from reactivity studies. This laboratory continues to pursue the isolation of NHC-stabilized main-group molecules in an effort to study their unusual structure and bonding motifs.

CHAPTER 4

EXPERIMENTAL

4.1. General Background

4.1.1 Techniques and Reagents

Unless otherwise noted, all manipulations were performed using a combination of standard Schlenk techniques and an MBraun inert atmosphere glovebox. Tetrahydrofuran, diethyl ether, and hexane were refluxed and distilled under an atmosphere of argon from a mixture of sodium metal and benzophenone. Toluene was refluxed and distilled over sodium metal. The Schlenk lines were protected under argon, which was first passed through copper-based purification and molecular sieve drying columns prior to use. Melting points were determined on a Haake Buchler MFB 595 802 C melting point apparatus.

Arsenic(III) chloride, gallium(III) chloride, borane-tetrahydrofuran complex solution ($\text{BH}_3\cdot\text{THF}$) in 1.0 M in THF, silicon(IV) chloride, glyoxal (40% aqueous solution), potassium tert-butoxide, and graphite were purchased from Aldrich Chemical Company (Milwaukee, WI). 2,6-diisopropylphenylaniline (92%) was purchased from Acros Organics (New Jersey, NJ). Chloromethylethyl ether (96%) was purchased from TCI America (Montgomeryville, PA). Potassium was purchased from Strem Chemicals (Newburyport, MA). All reagents were used without further purification.

4.1.2 Instrumental Measurements

^1H NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer . ^{11}B NMR spectra were recorded on a Varian Unity Inova 500 MHz spectrometer. Deuterated tetrahydrofuran (THF-d₈), dichloromethane (CD₂Cl₂), benzene (C₆D₆) and acetonitrile (CD₃CN) were used as the lock solvents in NMR experiments. EPR spectrum was recorded using an ESP-300D spectrometer (Bruker, Billerica, MA) equipped with an ER-4116 dual mode cavity. Spectral simulation was carried out using the EasySpin software package (<http://www.easyspin.org>).

4.1.2 X-ray Diffraction Methods

X-ray quality crystals were mounted in glass capillaries under argon atmosphere in a glovebox. The capillaries were temporarily sealed with silicon grease for removal from the glovebox to the bench top where they were flame sealed. The X-ray intensity data were collected at room temperature on a Bruker SMART APEX II X-ray diffractometer system with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) using the ω -scan technique. Solution refinement was performed using the SHELXTL 6.1 solution package. Data were corrected for polarization and Lorentz effects and integrated with the manufacturer's SAINT software. Data were corrected for absorption effects with the SADABS. Structures were solved using the SHELXTL 6.1 Software Package. Non-hydrogen atomic scattering factors were taken from literature tabulations. Non-hydrogen atoms were located from successive fourier map calculations and refined in anisotropic displacement parameters. Hydrogen atoms were allowed to ride on the carbon to which they are bonded assuming a C–H bond distance of 0.95 \AA . Hydrogen atom temperature

factors were fixed at 1.10 times the isotropic temperature factor on the carbon to which they are bonded.

4.2 Preparation of Starting Materials

4.2.1 *Synthesis of glyoxal-bis-(2,6-diisopropylphenyl)imine.*

This procedure was performed on the bench top according to the published procedure.⁸⁸ A 40% aqueous solution of glyoxal (108.9 g, 0.75 mol) was added to a flask containing 92% of 2,6-diisopropylaniline (321.4 g, 1.67 mol) and 1000 mL of n-propanol. Next, 350 mL of n-propanol and 300 mL of water was subsequently added and the solution was stirred for 16 hours, during which time a thick yellow precipitate formed. 1200 mL of water was added to the reaction mixture, which was filtered and dried in vacuo to give glyoxal-bis-(2,6-diisopropylphenyl)imine. The purity was confirmed by ¹H NMR.

4.2.2 *Synthesis of 1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride.*

This procedure was performed in the fume-hood according to the published procedure.⁸⁸ Glyoxal-bis-(2,6-diisopropylphenyl)imine (232.92 g, 0.62 mol) was added to 1200 mL of THF. A 96% solution of chloromethylethyl ether (63.7 g, 0.65 mol) in 100 mL of THF and 6 mL of water were added to the flask and stirred for 16 hours. (Note: chloromethylethyl ether is volatile, an irritant and a lachrymator (substance which increases the flow of tears). Therefore, it needs to be handled in the fume hood). The solution was stirred for 16 hours and filtered to give an off-white powder of 1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride. The purity was confirmed by ¹H NMR.

4.2.3 Synthesis of 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene.

1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride (25.0 g, 0.06 mol) was dried in vacuo in a Schlenk flask while stirring for 24 hours. It was transferred to a glovebox and potassium tert-butoxide (6.99 g, 0.062 mol) was added to it. Then 150 mL of dry THF was added to the flask and the mixture was stirred for 16 hours. The solvent was removed in vacuo and 200 mL of toluene was added to it. It was heated until all solid dissolved. The solution was filtered through celite and all solvent was removed in vacuo to give a pale yellow powder (19.38 g, 85% yield). Purity was confirmed by ^1H NMR.

4.2.4 Synthesis of Potassium Graphite.

Graphite (25.64 g, 2.14 mol) was dried in a flask in a 150 °C oven for 2 days. It was transferred to a glovebox and potassium (10.58 g, 0.27 mol) was cut into small pieces and added to the flask. It was heated until the mixture turned golden-brown (quantitative yield).

4.3 Syntheses of Carbene-Stabilized Diarsenic

*4.3.1 Synthesis of **1**.*

N-heterocyclic carbene ligand, :C{N(2,6-*i*Pr₂C₆H₃)CH}₂, (3.50 g, 9.01 mmol) was added to a flask containing 50 mL of hexane at ambient temperature. After the slurry was stirred for about 10 minutes, AsCl₃ (1.63 g, 8.99 mmol) was added into the flask. The mixture was stirred for 21 hours and the solvent was removed in vacuo leading to an off-white powder **1** (4.95 g, 96.5% yield). X-ray quality colorless crystals of **1** were isolated from toluene/THF at ambient temperature. Mp: gradually decomposes and melts at 324.2 °C. ^1H NMR (400MHz, C₆D₆): d 0.93 [d, 12H, CH(CH₃)₂], 1.54 [d, 12H, CH(CH₃)₂],

3.30 [m, 4H, $CH(CH_3)_2$], 6.47 (s, 2H, NCH), 7.08 (d, 4H, Ar-H), 7.18 (t, 2H, Ar-H).

Crystal data for **1**: $C_{27}H_{36}AsCl_3N_2$, fw = 569.85, monoclinic, $P2(1)/n$ (No. 14), $a = 11.0692(7)$ Å, $b = 13.8303(9)$ Å, $c = 19.2882(12)$ Å, $\alpha = 90.00^\circ$, $\beta = 104.3760(10)^\circ$, $\gamma = 90.00^\circ$, $V = 2860.4(3)$ Å³, $Z = 4$, $R1 = 0.0465$ for 3682 data ($I > 2s(I)$), $wR_2 = 0.1169$ (all data).

4.3.2 Synthesis of **2**.

Tetrahydrofuran (60 mL) was added to a flask containing **1** (4.95 g, 8.69 mmol) and KC_8 (3.52 g, 26.07 mmol). After stirring the mixture vigorously for 15 hours at ambient temperature, the solvent was removed in vacuo and the residue was extracted with hexane. The filtrate was concentrated to 4 mL and X-ray quality single red crystals of **2** were obtained overnight at ambient temperature (0.77 g, 19.2% yield). Mp: 216.5 °C. ¹H NMR (400MHz, C_6D_6): d 1.15 [d, 24H, $CH(CH_3)_2$], 1.49 [d, 24H, $CH(CH_3)_2$], 3.06 [m, 8H, $CH(CH_3)_2$], 6.12 (s, 4H, NCH), 7.05 (d, 8H, Ar-H), 7.19 (t, 4H, Ar-H). Crystal data for **2**: $C_{54}H_{72}As_2N_4$, fw = 927.0, triclinic, $P-1$ (No.2), $a = 10.842(4)$ Å, $b = 11.160(4)$ Å, $c = 12.592(5)$ Å, $\alpha = 95.640(5)^\circ$, $\beta = 112.601(5)^\circ$, $\gamma = 108.741(5)^\circ$, $V = 1288.6(9)$ Å³, $Z = 1$, $R1 = 0.0349$ for 4685 data ($I > 2s(I)$), $wR_2 = 0.0890$ (all data).

4.4 Syntheses of Oxidized Diarsenic Derivatives

4.4.1 Synthesis of $\mathbf{6}^+[GaCl_4]^-$.

Compound **2** (0.14 g, 0.15 mmol) was stirred in 30 mL of ether at ambient temperature over 10 min. Then $GaCl_3$ (0.05 g, 0.30 mmol) of was added in to the flask. The color of the solution turned dark green. After 16 h of stirring, the solution was filtered and the precipitate was rinsed with 100 mL of toluene. The residue was dried in

vacuo leading to the green powder **6**⁺[GaCl₄]⁻ (0.05 g, 29.1% yield). Dark green crystals of **6**⁺[GaCl₄]⁻ were obtained in 5 mL of THF/hexane (1:4) mixed solvent. Mp: melts at 313.3 °C. Crystal data for **6**⁺[GaCl₄]⁻: C₁₁₂H₁₅₂N₈O₁As₄Ga₂C₁₈, fw = 2349.14, monoclinic, C2/c, *a* = 24.040(8) Å, *b* = 27.149(10) Å, *c* = 22.396(8) Å, *V* = 12467(7) Å³. *Z* = 4, R1 = 0.0549 for 7862 data (I>2σ(I)), wR₂ = 0.1872 (all data).

4.6 Synthesis of **6**²⁺[GaCl₄]₂

Compound **2** (0.18 g, 0.19 mmol) was stirred in 30 mL of toluene at ambient temperature over 10 min. Then GaCl₃ (0.14 g, 0.76 mmol) was added in to the flask. The color of the solution turned dark green. Within 15 min, the green color faded and the solution turned orange. After 16 h of stirring, the solution was filtered and the precipitate was rinsed with 100 mL of toluene. The residue was dried in vacuo to give compound **6**²⁺[GaCl₄]₂ (quantitative yield). X-ray quality orange crystals of **6**²⁺[GaCl₄]₂ were obtained by slow evaporation of acetonitrile. Mp: melts at 214.7 °C. ¹H NMR (400 MHz, CD₃CN): δ 0.89 [d, 24H, CH(CH₃)₂], 1.14 [d, 24H, CH(CH₃)₂], 2.16 [m, 8H, CH(CH₃)₂], 7.38 [d, 8H, Ar-H], 7.56 [t, 4H, Ar-H], 8.28 [s, 4H, NCH]. Crystal data for **6**²⁺[GaCl₄]₂: C₅₈H₇₈N₆As₂Ga₂Cl₈, fw = 1432.14, monoclinic, P2(1)/c, *a* = 15.2173(10) Å, *b* = 18.3240(12) Å, *c* = 13.9424(9) Å, *V* = 3495.7(4) Å³. *Z* = 2, R1 = 0.0385 for 6058 data (I>2σ(I)), Wr₂ = 0.1045 (all data).

4.5 Syntheses of “push–pull” Stabilized Silylenes

4.5.1 *Synthesis of 8.*

Compound **7** was prepared as previously described.⁶³ Pure crystals of **7** (1.19 g, 1.43 mmol) was stirred in 18 mL of toluene at ambient temperature over 10 min. Then 1.0 M BH₃.THF (5.72 mL, 5.72 mmol) was added in to the flask using a syringe. The color of the solution turned into brown-orange immediately. After 16 h stirring, the solvent was removed in vacuo. The resulting residue was dissolved in 5 mL of THF/hexane (1:4) mixed solvent and then concentrated to 2 mL, giving **8** as colorless crystals (0.91 g, 71.7% yield). Mp: melts at 181.7 °C. ¹H NMR (500 MHz, THF-d₈): δ -0.29 [br, 7H, B₃H₇], 0.98 [d, 6H, CH(CH₃)₂], 1.00 [d, 6H, CH(CH₃)₂], 1.04 [d, 6H, CH(CH₃)₂], 1.08 [d, 6H, CH(CH₃)₂], 1.11 [d, 6H, CH(CH₃)₂], 1.16 [d, 6H, CH(CH₃)₂], 1.18 [d, 6H, CH(CH₃)₂], 1.22 [d, 6H, CH(CH₃)₂], 2.46 [m, 2H, CH(CH₃)₂], 2.52 [m, 2H, CH(CH₃)₂], 2.73 [m, 2H, CH(CH₃)₂], 2.82 [m, 2H, CH(CH₃)₂], 2.89 [d, 1H, SiH], 3.13 [t, 2H, SiH₂], 7.12-7.42 [m, 12H, Ar-H], 7.26 [s, 2H, NCH], 7.55 [s, 2H, NCH]. ¹¹B NMR (160 MHz, THF-d₈): δ -50.42 [t, ¹J_B-H = 93 Hz, BH₂], -29.91 [m, ¹J_B-H = 34 Hz, B₃H₇]. Crystal data for **8**: C₁₂₀H₁₉₂N₈O₃B₈Si₄, fw = 1993.66, monoclinic, P21/n, *a* = 13.9722(16) Å, *b* = 22.691(3) Å, *c* = 21.080(2) Å, *V* = 6650.3(13) Å³. *Z* = 2, R1 = 0.0871 for 5220 data (I>2σ(I)), wR₂ = 0.2604 (all data)

4.5.2 *Synthesis of 9.*

A mixture (2.91 g) of compound **7** (3.20 mmol) and free NHC ligand (0.64 mmol) (5:1; characterized by the ¹H NMR spectrum), provided by rinsing the raw compound **7** material using hexane, was stirred in 35 mL of toluene at ambient temperature over 10 min. Then 1.0 M BH₃.THF (13.99 mL, 13.99 mmol) was added into the flask using a

syringe. The color of the solution turned immediately into brown-orange with the formation of considerable amount of precipitate. The mixture was stirred for 16 h, resulting in the isolation of both compound **8** (0.86 g, 30.3% yield) and **9** (1.5 g, 28.2% yield). The precipitate was filtered and then dissolved in 5 mL of DME/THF/hexane mixed solvent. Overnight X-ray quality colorless crystals of **9** were obtained. Mp: melts at 281.5 °C. After removing the toluene solvent of the filtrate in vaccuo, the residue was dissolved in 5 mL of THF/hexane (1:4) mixed solvent and then concentrated to 2 mL in vaccuo. Overnight X-ray quality colorless crystals of **9** were obtained. ¹H NMR (400 MHz, CD₂Cl₂): δ 0.86 [d, 6H, CH(CH₃)₂], 1.01 [d, 6H, CH(CH₃)₂], 1.04 [d, 12H, CH(CH₃)₂], 1.16 [d, 12H, CH(CH₃)₂], 1.18 [d, 6H, CH(CH₃)₂], 1.21 [d, 6H, CH(CH₃)₂], 2.44 [m, 4H, CH(CH₃)₂], 2.88 [m, 2H, CH(CH₃)₂], 3.10 [m, 2H, CH(CH₃)₂], 3.18 [s, 2H, SiC₂H₂], 7.07-7.44 [m, 12H, Ar-H], 7.18 [s, 2H, NCH]. ¹¹B NMR (160 MHz, CD₂Cl₂): δ -35.25 [q, 1J_{BB}-H = 87 Hz, CBH₃], -46.83 [broad doublet (bd) with shoulders, ¹J_{BB}-H = 82 Hz, SiBH₃]. Crystal data for **9**: C₅₈H₈₈N₄O₂B₂Si, fw = 923.03, orthorhombic, Pna2, *a* = 20.195(6) Å, *b* = 12.590(4) Å, *c* = 22.879(6) Å, *V* = 5817(3) Å³, *Z* = 4, R1 = 0.0520 for 6968 data (I>2σ(I)), wR₂ = 0.1357 (all data).

REFERENCES

- (1) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463-3503.
- (2) Crudden, C. M.; Edwards, D. *Eur. J. Org. Chem.* **2003**, 4695-4712.
- (3) Omae, I. *Applications of Organometallic Compounds*; Wiley: West Sussex, 1998.
- (4) Eisch, J. J. *The Chemistry of Organometallic Compounds: the Main Group Elements*; Macmillan Publishers: New York, 1967.
- (5) Thayer, J. S. *Organometallic Chemistry An Overview*; VCH publishers: New York, 1988.
- (6) Guan, Z. *Metal Catalysts in Olefin Polymerization*; Springer: Berlin, 2009.
- (7) Jaouen, G.; Metzler-Nolte, N. *Medicinal Organometallic Chemistry*; Springer: Heidelberg, 2010.
- (8) Seydel, D. *Organometallics* **2001**, *20*, 1488-1498.
- (9) Thayer, J. S. *J. Chem. Educ.* **1966**, *43*, 594-595.
- (10) Spessard, O. G.; Miessler, L. G. *Organometallic Chemistry*; Prentice-Hall: New Jersey, 1996.
- (11) Seydel, D. *Organometallics* **2001**, *20*, 2-6.
- (12) Wunderlich, J. A.; Mellor, D. P. *Acta Crystallogr* **1954**, *7*, 130.
- (13) Frankland, E. *Liebigs Ann.* **1849**, 171-213.
- (14) Jones, P. R.; Southwick, E. *J. Chem. Educ.* **1970**, *47*.
- (15) Seydel, D. *Organometallics* **2009**, *28*, 1598-1605.
- (16) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039-1040.

- (17) Miller, S. A.; Tebboth, J. A.; Tremaine, J. F. *J. Chem. Soc.* **1952**, 632-635.
- (18) Fischer, E. O.; Pfab, W. *Z. Naturforsch. B* **1952**, 7, 377-379.
- (19) Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, 74, 2125-2126.
- (20) Dunitz, J. D.; Orgel, L. E.; Rich, A. *Acta Cryst.* **1956**, 9, 373-375.
- (21) *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A.; Salzer, A., Eds.; Thieme Medical Publishers, Inc.: New York, 1996; Vol. 1:Literature, Laboratory techniquesand Common Starting Materials.
- (22) Daly, J. J. *J. Chem. Soc.* **1964**, 6147-6166.
- (23) Rheingold, A. L.; Sullivan, P. J. *Organometallics* **1983**, 2, 327-331.
- (24) Pitzer, K. S. *J. Am. Chem. Soc.* **1948**, 70, 2140-2145.
- (25) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, 72, 4493-4503.
- (26) Goubeau, J. *Angew. Chem.* **1957**, 69, 77-82.
- (27) Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1976**, 261-262.
- (28) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, 214, 1343-1344.
- (29) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, 103, 4587-4589.
- (30) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268-2274.
- (31) Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. *Angew. Chem. Int. Ed.* **2002**, 41, 2842-2844.

- (32) Wright, R. J.; Phillips, A. D.; Hardman, N. J.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 8538-8539.
- (33) Fink, M. J.; Michalczuk, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Chem. Soc., Chem. Commun.* **1983**, 1010-1111.
- (34) Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480-482.
- (35) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275-324.
- (36) Stürmann, M.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Angew. Chem. Int. Ed.* **1999**, *38*, 187-189.
- (37) Stürmann, M.; Weidenbruch, M.; Klinkhammer, K.; Lissner, F.; Marsmann, H. *Organometallics* **1988**, *17*, 4425-4428.
- (38) Twamley, B.; Sofield, C. D.; Omlstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1999**, *121*, 3357-3367.
- (39) Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Pakulski, M. *J. Am. Chem. Soc.* **1983**, *105*, 5506-5507.
- (40) Cowley, A. H.; Nicholas, N. C.; Pakulski, M. *J. Chem. Soc., Dalton Trans.* **1985**, 383-386.
- (41) Tokitoh, N.; Arai, Y.; Sasamori, T.; Okazaki, R.; Nagase, S.; Uekusa, H.; Soashi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 433-434.
- (42) Tokitoh, N.; Arai, Y.; Okazaki, R.; Nagase, S. *Science* **1997**, *277*, 78-80.
- (43) Power, P. P. *J. Chem. Soc., Dalton Trans.* **1998**, 2939-2951.
- (44) Clyburne, J. A. C.; McMullen, N. *Coord. Chem. Rev.* **2000**, *210*, 73-99.
- (45) Rivard, E.; Power, P. P. *Inorg. Chem.* **2007**, *46*, 10047-10064.

- (46) Wang, Y.; Robinson, G. H. *Organometallics* **2007**, *26*, 2-11.
- (47) Wang, Y.; Robinson, G. H. *Chem. Commun.* **2009**, 5201-5213.
- (48) Lee, V. Y.; Sekiguchi, A. *Organometallic Compounds of Low-coordinate Si, Ge, Sn and Pb*; John Wiley & Sons, Ltd: West Sussex, UK, 2010.
- (49) Su, J.; Li, X.-W.; Crittendon, R. C.; Robinson, G. H. *J. Am. Chem. Soc.* **1997**, *119*, 5471-5472.
- (50) Wright, R. J.; Brynda, M.; Power, P. P. *Angew. Chem. Int. Ed.* **2006**, *45*, 5953-5956.
- (51) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. *Science* **2004**, *305*, 1755-1757.
- (52) Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1785-1787.
- (53) Sugiyama, Y.; Sasamori, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 1023-1031.
- (54) Phillips, A. D.; Wright, R. J.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 5930-5931.
- (55) Pu, L.; Twamley, B.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 3524-3525.
- (56) Kleiner, N.; Dräger, M. *J. Organomet. Chem.* **1984**, *270*, 151-170.
- (57) Chen, Y.; Hartmann, M.; Diedenhofen, M.; Frenking, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2052-2055.
- (58) Linti, G.; Köster, W.; Piotrowski, H.; Rodig, A. *Angew. Chem. Int. Ed.* **1998**, *37*, 2209-2211.
- (59) Bytheway, I.; Lin, Z. *J. Am. Chem. Soc.* **1998**, *120*, 12133-12134.
- (60) Pyykkö, P.; Riedel, S.; Patzschke, M. *Chem. Eur. J.* **2005**, *11*, 3511-3520.

- (61) Xie, Y.; Grev, R. S.; Gu, J.; Schaefer, H. F.; Schleyer, P. v. R.; Su, J.; Li, X.-W.; Robinson, G. H. *J. Am. Chem. Soc.* **1998**, *120*, 3773-3780.
- (62) Xie, Y.; Schaefer, H. F.; Robinson, G. H. *Chem. Phys. Lett.* **2000**, *317*, 174-180.
- (63) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *Science* **2008**, *321*, 1069-1071.
- (64) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2008**, *130*, 14970-14971.
- (65) Abraham, M. Y.; Wang, Y.; Xie, Y.; Wei, P.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *Chem. Eur. J.* **2010**, *16*, 432-435.
- (66) Buchner, E.; Curtius, T. *Ber. Dtsch. Chem. Ges.* **1885**, *8*, 2371-2377.
- (67) Staudinger, H.; Kupfer, O. *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 501-509.
- (68) Doering, W. v. E.; Hoffmann, A. K. *J. Am. Chem. Soc.* **1954**, *76*, 6162-6165.
- (69) Breslow, R. *J. Am. Chem. Soc.* **1958**, *80*, 3719-3726.
- (70) Wanzlick, H. W. *Angew. Chem.* **1962**, *74*, 129-134.
- (71) Igau, A.; Grutzmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463-6466.
- (72) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361-363.
- (73) Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290-309.
- (74) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370-2375.
- (75) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39-91.

- (76) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485-1499.
- (77) Wang, Y.; Robinson, G. H. *Inorg. Chem.* **2011**, *50*, 12326-12337.
- (78) Martin, D.; Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Organometallics* **2011**, *30*, 5304-5313.
- (79) Wang, Y.; Robinson, G. H. *Dalton Trans.* **2012**, *41*, 337-345.
- (80) Wilson, D. J. D.; Couchman, S. A.; Dutton, J. L. *Inorg. Chem.* **2012**, *51*, 7657-7668.
- (81) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565-1604.
- (82) Doetz, K. H.; Stendel, J. *Chem. Rev.* **2009**, *109*, 3227-3274.
- (83) Wanzlick, H. W.; Schoenherr, H. J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 141-142.
- (84) Oefele, K. *J. Organomet. Chem.* **1968**, *12*, P42-P43.
- (85) Wanzlick, H. W.; Schikora, E. *Angew. Chem.* **1960**, *72*, 494.
- (86) Denk, M. K.; Hatano, K.; Ma, M. *Tetrahedron Lett.* **1999**, *40*, 2057-2060.
- (87) Schoenherr, H. J.; Wanzlick, H. W. *Justus Liebigs Ann. Chem.* **1970**, *731*, 176-179.
- (88) Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523-14534.
- (89) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 8810-8849.
- (90) Lavallo, V.; Canac, Y.; Prasang, C.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 5705-5709.

- (91) Grigsby, W. J.; Power, P. *Chem. Eur. J.* **1997**, *3*, 368-375.
- (92) Moezzi, A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 2715-2717.
- (93) Moezzi, A.; Bartlett, R. A.; Power, P. P. *Angew. Chem. Int. Ed.* **1992**, *104*, 1082-1083.
- (94) Noth, H.; Knizek, J.; Ponikwar, W. *Eur. J. Inorg. Chem.* **1999**, 1931-1937.
- (95) Wang, Y.; Quillian, B.; Wei, P.; Wannere, C. S.; Xie, Y.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2007**, *129*, 12412-12413.
- (96) Smith, J. G.; Ho, I. *J. Org. Chem.* **1972**, *37*, 4260-4264.
- (97) Cheng, T. C.; Headley, L.; Halasa, A. F. *J. Am. Chem. Soc.* **1971**, *93*, 1502-1503.
- (98) Garst, J. F. *Acc. Chem. Res.* **1971**, *4*, 400-406.
- (99) Wang, Z.-X.; Chen, Z.; Jiao, H.; Schleyer, P. v. R. *J. Theoret. Comput. Chem.* **2005**, *4*, 669-688.
- (100) Wang, Y.; Quillian, B.; Wei, P.; Xie, Y.; Wannere, C. S.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2008**, *130*, 3298-3299.
- (101) Giju, K. T.; Phukan, A. K.; Jemmis, E. D. *Angew. Chem. Int. Ed.* **2003**, *42*, 539-542.
- (102) Zhou, M.; Tsumori, N.; Li, Z.; Fan, K.; Andrews, L.; Xu, Q. *J. Am. Chem. Soc.* **2002**, *124*, 12936-12937.
- (103) Li, S.-D.; Zhai, H.-J.; Wang, L.-S. *J. Am. Chem. Soc.* **2008**, *130*, 2573-2579.
- (104) Ducati, L. C.; Takagi, N.; Frenking, G. *J. Phys. Chem. A* **2009**, *113*, 11693-11698.

- (105) Papakondylis, A.; Miliordos, E.; Mavridis, A. *J. Phys. Chem. A.* **2004**, *108*, 4335-4340.
- (106) Mitoraj, M. P.; Michalak, A. *Inorg. Chem.* **2011**, *50*, 2168-2174.
- (107) Holzmann, N.; Stasch, A.; Jones, C.; Frenking, G. *Chem. Eur. J.* **2011**, *17*, 13517-13525.
- (108) Braunschweig, H.; Dewhurst, R. D.; Hammond, K.; Mies, J.; Radacki, K.; Vargas, A. *Science* **2012**, *336*, 1420-1422.
- (109) Kaufmann, E.; Schleyer, P. v. R. *Inorg. Chem.* **1988**, *27*, 3987-3992.
- (110) Kinjo, R.; Donnadieu, B.; Celik, M. A.; Frenking, G.; Bertrand, G. *Science* **2011**, *333*, 610-613.
- (111) Hassanzadeh, P.; Andrews, L. *J. Phys. Chem.* **1993**, *97*, 4910-4915.
- (112) Bettinger, H. F. *J. Am. Chem. Soc.* **2006**, *128*, 2534-2535.
- (113) Braunschweig, H.; Dewhurst, R. D.; Schneider, A. *Chem. Rev.* **2010**, *110*, 3924-3957.
- (114) Bissinger, P.; Braunschweig, H.; Kraft, K.; Kupfer, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 4704-4707.
- (115) Fischer, R. C.; Power, P. P. *Chem. Rev.* **2010**, *110*, 3877-3923.
- (116) Quillian, B.; Wei, P.; Wannere, C. S.; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2009**, *131*, 3168-3169.
- (117) Jones, C.; Junk, P. C.; Kloth, M.; Proctor, K. M.; Stasch, A. *Polyhedron* **2006**, *25*, 1592-1600.
- (118) Loos, D.; Baum, E.; Ecker, A.; Schnockel, H.; Downs, A. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 860-862.

- (119) Linti, G.; Coban, S.; Dutta, D. *Z. Anorg. Allg. Chem.* **2004**, *630*, 319-323.
- (120) Wade, K. *J. Chem. Soc. Chem. Comm.* **1971**, 792-793.
- (121) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311-319.
- (122) Dong, Z.-C.; Corbett, J. D. *Inorg. Chem.* **1996**, *35*, 2301-2306.
- (123) Mandal, S. K.; Roesky, H. W. *Chem. Commun.* **46**, 6016-6041.
- (124) Pak, C.; Rienstra-Kiracofe, J. C.; Schaefer, H. F., III *J. Phys. Chem. A* **2000**, *104*, 11232-11242.
- (125) Nimlos, M. R.; Harding, L. B.; Ellison, G. B. *J. Chem. Phys.* **1987**, *87*, 5116-5124.
- (126) Zhou, M.; Jiang, L.; Xu, Q. *J. Chem. Phys.* **2004**, *121*, 10474-10482.
- (127) Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Frenking, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 9701-9704.
- (128) Jones, C.; Sidiropoulos, A.; Holzmann, N.; Frenking, G.; Stasch, A. *Chem. Commun.* **2012**, *48*, 9855-9857.
- (129) Dyker, C. A.; Lavallo, V.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 3206-3209.
- (130) Fuerstner, A.; Alcarazo, M.; Goddard, R.; Lehmann, C. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 3210-3214.
- (131) Tonner, R.; Oexler, F.; Neumueller, B.; Petz, W.; Frenking, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 8038-8042.
- (132) Tonner, R.; Frenking, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 8695-8698.
- (133) Dutton, J. L.; Wilson, D. J. D. *Angew. Chem., Int. Ed.* **2011**, *51*, 1477-1480.

- (134) King, B. R. *Inorganic Chemistry of the Main Group Elements*; VCH: New York, 1995.
- (135) Du Mont, W.-W.; Gust, T.; Seppala, E.; Wismach, C. *J. Organomet. Chem.* **2004**, *689*, 1331-1336.
- (136) Schafer, H.; Nickl, J. *Z. Anorg. Allg. Chem.* **1953**, *274*, 250-64.
- (137) Teichmann, R.; Wolf, E. *Z. Anorg. Allg. Chem.* **1966**, *347*, 145-155.
- (138) Schaefer, H.; Bruderreck, H.; Morcher, B. *Z. Anorg. Allg. Chem.* **1967**, *352*, 122-137.
- (139) Jutzi, P.; Kanne, D.; Kruger, C. *Angew. Chem.* **1986**, *98*, 163-164.
- (140) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691-2692.
- (141) Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704-714.
- (142) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354-396.
- (143) Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457-492.
- (144) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, *121*, 9722-9723.
- (145) Filippou, A. C.; Chernov, O.; Schnakenburg, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 5687-5690.
- (146) Koe, J. R.; Powell, D. R.; Buffy, J. J.; Hayase, S.; West, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1441-1442.
- (147) Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 5683-5686.

- (148) Boesveld, W. M.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Schleyer, P. v. R. *Chem. Commun.* **1999**, 755-756.
- (149) Wiberg, N.; Wagner, G.; Riede, J.; Mueller, G. *Organometallics* **1987**, *6*, 32-35.
- (150) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741-8753.
- (151) So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 3948-3950.
- (152) Sen, S. S.; Khan, S.; Samuel, P. P.; Roesky, H. W. *Chem. Sci.* **2012**, *3*, 659-682.
- (153) Bock, H.; Mueller, H. *Inorg. Chem.* **1984**, *23*, 4365-4368.
- (154) Esterhuysen, C.; Frenking, G. *Theor. Chem. Acc.* **2004**, *111*, 381-389.
- (155) Piro, N. A.; Figueroa, J. S.; McKellar, J. T.; Cummins, C. C. *Science* **2006**, *313*, 1276-1279.
- (156) Back, O.; Kuchenbeiser, G.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2009**, *48*, 5530-5533.
- (157) Cossairt, B. M.; Piro, N. A.; Cummins, C. C. *Chem. Rev.* **2010**, *110*, 4164-4177.
- (158) Caporali, M.; Gonsalvi, L.; Rossin, A.; Peruzzini, M. *Chem. Rev.* **2010**, *110*, 4178-4235.
- (159) Scheer, M.; Balazs, G.; Seitz, A. *Chem. Rev.* **2010**, *110*, 4236-4256.
- (160) Masuda, J. D.; Schoeller, W. W.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2007**, *129*, 14180-14181.
- (161) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, *2*, 389-399.
- (162) Cotton, F. A.; Wilkinson, G.; Bochmann, M.; Murillo, C. *Advanced Inorganic Chemistry*; 6th ed.; Wiley: New York, 1998.

- (163) Dasent, W. E. *Inorganic Energetics: An Introduction*. 2nd Ed; Cambridge University Press: Cambridge, 1982.
- (164) Mochizuki, Y.; Tanaka, K. *Chem. Phys. Lett.* **1997**, 274, 264-268.
- (165) Roy, D.; Navarro-Vazquez, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2009**, 131, 13045-13053.
- (166) Huttner, G.; Sigwarth, B.; Scheidsteiger, O.; Zsolnai, L.; Orama, O. *Organometallics* **1985**, 4, 326-332.
- (167) Scherer, O. J.; Ehses, M.; Wolmershauser, G. *Angew. Chem. Int. Ed.* **1998**, 37, 507-510.
- (168) Masuda, J. D.; Schoeller, W. W.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2007**, 46, 7052-7055.
- (169) Williams, D. J.; Quicksall, C. O.; Wynne, K. J. *Inorg. Chem.* **1978**, 17, 2071-2073.
- (170) Webster, M.; Keats, S. *J. Chem. Soc. A.* **1971**, 836-838.
- (171) Maxwell, L. R.; Hendricks, S. B.; Mosley, V. M. *J. Chem. Phys.* **1935**, 3, 699-709.
- (172) Pykkoe, P.; Atsumi, M. *Chem. Eur. J.* **2009**, 15, 186-197.
- (173) Arduengo, A. J., III; Calabrese, J. C.; Cowley, A. H.; Dias, H. V. R.; Goerlich, J. R.; Marshall, W. J.; Riegel, B. *Inorg. Chem.* **1997**, 36, 2151-2158.
- (174) Wang, Y.; Xie, Y.; Abraham, M. Y.; Wei, P.; Schaefer, H. F.; Schleyer, P. v. R.; Robinson, G. H. *Chem. Commun.* **2011**, 47, 9224-9226.
- (175) Hicks, R. G.; Editor *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds*; Wiley: Chichester, U.K., 2010.

- (176) Back, O.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. *Nat. Chem.* **2010**, *2*, 369-373.
- (177) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Chem. Commun.* **1976**, 623-624.
- (178) Agarwal, P.; Piro, N. A.; Meyer, K.; Mueller, P.; Cummins, C. C. *Angew. Chem. Int. Ed.* **2007**, *46*, 3111-3114.
- (179) Ishida, S.; Hirakawa, F.; Iwamoto, T. *J. Am. Chem. Soc.* **2011**, *133*, 12968-12971.
- (180) Back, O.; Celik, M. A.; Frenking, G.; Melaimi, M.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2010**, *132*, 10262-10263.
- (181) Sasamori, T.; Mieda, E.; Nagahora, N.; Sato, K.; Shiomi, D.; Takui, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 12582-12588.
- (182) Hinchley, S. L.; Morrison, C. A.; Rankin, D. W. H.; Macdonald, C. L. B.; Wiacek, R. J.; Voigt, A.; Cowley, A. H.; Lappert, M. F.; Gundersen, G.; Clyburne, J. A. C.; Power, P. P. *J. Am. Chem. Soc.* **2001**, *123*, 9045-9053.
- (183) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Dalton Trans.* **1980**, 2428-2433.
- (184) Wulfsberg, G. *Principles of Descriptive Inorganic Chemistry*; Brooks/Cole: Monterey, CA, 1987.
- (185) Xu, Y.-J.; Zhang, Y.-F.; Li, J.-Q. *Chem. Phys. Lett.* **2006**, *421*, 36-41.
- (186) Takeuchi, K.; Ikoshi, M.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2010**, *132*, 930-931.
- (187) Takeuchi, K.; Ichinohe, M.; Sekiguchi, A. *Organometallics* **2011**, *30*, 2044-2050.

- (188) Abraham, M. Y.; Wang, Y.; Xie, Y.; Wei, P.; Schaefer, H. F.; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2011**, *133*, 8874-8876.
- (189) Yoon, C. W.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **2009**, *131*, 855-864.
- (190) Bishop, V. L.; Kodama, G. *Inorg. Chem.* **1981**, *20*, 2724-2727.
- (191) Mebel, A. M.; Musaev, D. G.; Morokuma, K. *Chem. Phys. Lett.* **1993**, *214*, 69-76.
- (192) Dubois, I.; Herzberg, G.; Verma, R. D. *J. Chem. Phys.* **1967**, *47*, 4262-4263.
- (193) Yamada, C.; Kanamori, H.; Hirota, E.; Nishiwaki, N.; Itabashi, N.; Kato, K.; Goto, T. *J. Chem. Phys.* **1989**, *91*, 4582-4586.
- (194) Koecher, T.; Kerst, C.; Friedrichs, G.; Temps, F. In *Silicon Chemistry*; Jutzi, P., Schubert, U., Eds.; Wiley-VCH: Weinheim, 2003, p 44-57.
- (195) Al-Rafia, S. M. I.; Malcolm, A. C.; Liew, S. K.; Ferguson, M. J.; Rivard, E. *J. Am. Chem. Soc.* **2011**, *133*, 777-779.
- (196) Thimer, K. C.; Al-Rafia, S. M. I.; Ferguson, M. J.; McDonald, R.; Rivard, E. *Chem. Commun.* **2009**, 7119-7121.
- (197) Inoue, S.; Driess, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 5614-5615.
- (198) Bharatam, P. V.; Moudgil, R.; Kaur, D. *Organometallics* **2002**, *21*, 3683-3690.
- (199) Kajiwara, T.; Takeda, N.; Sasamori, T.; Tokitoh, N. *Organometallics* **2004**, *23*, 4723-4734.
- (200) Takeda, N.; Kajiwara, T.; Tokitoh, N. *Chem. Lett.* **2001**, 1076-1077.
- (201) Arp, H.; Marschner, C.; Baumgartner, J. *Dalton Trans.* **2010**, *39*, 9270-9274.
- (202) Maier, G.; Reisenauer, H. P.; Egenolf, H. *Eur. J. Org. Chem.* **1998**, 1313-1317.
- (203) Maier, G.; Reisenauer, H. P. *Eur. J. Org. Chem.* **2003**, 479-487.

(204) Maier, G.; Reisenauer, H. P. *Eur. J. Org. Chem.* **2003**, 488-491.

Structural Data for L¹:AsCl₃ **1** (L¹: = :C{N(2,6-*i*Pr₂C₆H₃)CH}₂).

Table 7. Crystal data and structural refinement for **1**.

Empirical formula	C ₂₇ H ₃₆ AsCl ₃ N ₂
Formula weight	569.85
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 11.0692(7) Å b = 13.8303(9) Å c = 19.2882(12) Å α = 90° β = 104.3760(10)° γ = 90°
Volume	2860.4(3) Å ³
Z, Calculated density	4, 1.323 Mg/m ³
Absorption coefficient	1.486 mm ⁻¹
F(000)	1184
Crystal size	0.13 x 0.11 x 0.06 mm
Theta range for data collection	2.18 to 27.87 deg.
Limiting indices	-14<=h<=14, -18<=k<=18, -25<=l<=25
Reflections collected / unique	37448 / 6829 [R(int) = 0.0830]
Completeness to theta =	27.87 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9161 and 0.8303
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6829 / 42 / 335
Goodness-of-fit on F ²	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0465, wR2 = 0.0922
R indices (all data)	R1 = 0.1205, wR2 = 0.1170
Largest diff. peak and hole	0.366 and -0.435 e. Å ⁻³

Table 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**.

Atom	X	Y	Z	U (eq)
As(1)	454(1)	3558(1)	1949(1)	44(1)
Cl(1)	1718(1)	2769(1)	2802(1)	66(1)
Cl(2)	-1266(3)	2499(3)	2128(2)	70(1)
Cl(3)	2097(2)	4557(3)	1808(2)	73(1)
As(1')	624(7)	3420(5)	2218(3)	44(1)
Cl(1')	-184(6)	3429(5)	1090(3)	59(2)
Cl(2')	2368(14)	4342(15)	2068(11)	89(6)
Cl(3')	-1180(20)	2532(16)	2352(13)	75(6)
N(1)	-1036(2)	5211(2)	2202(1)	37(1)
N(2)	222(2)	4869(2)	3221(1)	36(1)
C(1)	-125(3)	4597(2)	2527(2)	33(1)
C(2)	-1269(3)	5866(3)	2690(2)	51(1)
C(3)	-500(3)	5648(3)	3320(2)	51(1)
C(4)	1133(3)	4452(2)	3819(2)	37(1)
C(5)	2331(3)	4839(3)	4005(2)	45(1)
C(6)	3139(4)	4452(3)	4607(2)	66(1)
C(7)	2766(4)	3741(3)	5002(2)	73(1)
C(8)	1588(4)	3374(3)	4811(2)	62(1)
C(9)	718(3)	3728(2)	4210(2)	46(1)
C(10)	-614(4)	3355(3)	4025(2)	60(1)
C(11)	-1364(5)	3893(5)	4465(3)	130(3)
C(12)	-671(5)	2268(3)	4117(3)	106(2)
C(13)	2744(3)	5654(3)	3590(2)	56(1)
C(14)	2714(6)	6620(3)	3969(3)	102(2)
C(15)	4044(4)	5458(4)	3472(2)	91(2)
C(16)	-1670(3)	5228(2)	1442(2)	39(1)
C(17)	-1133(3)	5785(3)	990(2)	50(1)
C(18)	-1755(4)	5768(3)	267(2)	64(1)
C(19)	-2820(4)	5244(3)	22(2)	67(1)
C(20)	-3346(3)	4750(3)	487(2)	56(1)
C(21)	-2797(3)	4734(2)	1219(2)	42(1)
C(22)	-3452(3)	4257(3)	1732(2)	50(1)
C(23)	-4192(4)	3350(3)	1429(2)	72(1)
C(24)	-4324(4)	4970(3)	1963(2)	75(1)
C(25)	1(4)	6426(3)	1265(2)	66(1)
C(26)	829(4)	6508(4)	733(3)	103(2)
C(27)	-420(5)	7446(3)	1423(3)	98(2)

Table 9. Bond lengths [Å] for **1**.

Atoms	Distance	Atoms	Distance
As(1)-C(1)	2.018(3)	C(7)-C(8)	1.362(6)
As(1)-Cl(1)	2.1706(15)	C(8)-C(9)	1.399(5)
As(1)-Cl(3)	2.353(3)	C(9)-C(10)	1.518(5)
As(1)-Cl(2)	2.494(3)	C(10)-C(11)	1.521(6)
As(1')-C(1)	1.984(8)	C(10)-C(12)	1.517(6)
As(1')-Cl(1')	2.136(8)	C(13)-C(14)	1.526(6)
As(1')-Cl(3')	2.409(15)	C(13)-C(15)	1.536(5)
As(1')-Cl(2')	2.391(14)	C(16)-C(17)	1.400(5)
N(1)-C(1)	1.349(4)	C(16)-C(21)	1.393(4)
N(1)-C(2)	1.376(4)	C(17)-C(18)	1.395(5)
N(1)-C(16)	1.460(4)	C(17)-C(25)	1.521(5)
N(2)-C(1)	1.352(4)	C(18)-C(19)	1.364(5)
N(2)-C(3)	1.383(4)	C(19)-C(20)	1.369(5)
N(2)-C(4)	1.449(4)	C(20)-C(21)	1.392(5)
C(2)-C(3)	1.333(5)	C(21)-C(22)	1.515(5)
C(4)-C(5)	1.393(4)	C(22)-C(24)	1.521(5)
C(4)-C(9)	1.399(4)	C(22)-C(23)	1.533(5)
C(5)-C(6)	1.386(5)	C(25)-C(26)	1.540(5)
C(5)-C(13)	1.518(5)	C(25)-C(27)	1.539(6)
C(6)-C(7)	1.370(5)		

Table 10. Bond angles [°] for **1**.

Atoms	Angle	Atoms	Angle
C(1)-As(1)-Cl(1)	99.91(10)	C(6)-C(5)-C(13)	120.9(3)
C(1)-As(1)-Cl(3)	90.35(14)	C(7)-C(6)-C(5)	121.5(4)
Cl(1)-As(1)-Cl(3)	90.69(8)	C(8)-C(7)-C(6)	121.2(4)
C(1)-As(1)-Cl(2)	89.04(13)	C(7)-C(8)-C(9)	120.7(4)
Cl(1)-As(1)-Cl(2)	88.30(10)	C(4)-C(9)-C(8)	116.5(3)
Cl(3)-As(1)-Cl(2)	178.72(13)	C(4)-C(9)-C(10)	123.1(3)
C(1)-As(1')-Cl(1')	101.6(3)	C(8)-C(9)-C(10)	120.3(3)
C(1)-As(1')-Cl(3')	88.1(7)	C(11)-C(10)-C(12)	112.0(4)
Cl(1')-As(1')-Cl(3')	87.9(7)	C(11)-C(10)-C(9)	109.6(3)
C(1)-As(1')-Cl(2')	90.5(7)	C(12)-C(10)-C(9)	112.0(4)
Cl(1')-As(1')-Cl(2')	91.2(5)	C(5)-C(13)-C(14)	110.6(3)
Cl(3')-As(1')-Cl(2')	178.2(8)	C(5)-C(13)-C(15)	111.3(4)
C(1)-N(1)-C(2)	110.0(3)	C(14)-C(13)-C(15)	111.0(4)
C(1)-N(1)-C(16)	126.5(3)	C(17)-C(16)-C(21)	124.3(3)
C(2)-N(1)-C(16)	123.5(3)	C(17)-C(16)-N(1)	117.4(3)
C(1)-N(2)-C(3)	108.8(3)	C(21)-C(16)-N(1)	118.2(3)
C(1)-N(2)-C(4)	130.3(3)	C(16)-C(17)-C(18)	115.7(3)
C(3)-N(2)-C(4)	120.8(3)	C(16)-C(17)-C(25)	123.1(3)
N(1)-C(1)-N(2)	106.3(3)	C(18)-C(17)-C(25)	121.1(4)
N(1)-C(1)-As(1)	119.7(2)	C(17)-C(18)-C(19)	121.6(4)
N(2)-C(1)-As(1)	134.0(2)	C(20)-C(19)-C(18)	120.7(4)
N(1)-C(1)-As(1')	134.2(3)	C(19)-C(20)-C(21)	121.6(4)
N(2)-C(1)-As(1')	119.3(3)	C(16)-C(21)-C(20)	115.9(3)
As(1)-C(1)-As(1')	15.51(16)	C(16)-C(21)-C(22)	123.4(3)
C(3)-C(2)-N(1)	106.9(3)	C(20)-C(21)-C(22)	120.7(3)
C(2)-C(3)-N(2)	108.1(3)	C(21)-C(22)-C(24)	110.5(3)
C(5)-C(4)-C(9)	123.7(3)	C(21)-C(22)-C(23)	113.8(3)
C(5)-C(4)-N(2)	118.8(3)	C(24)-C(22)-C(23)	108.9(3)
C(9)-C(4)-N(2)	117.3(3)	C(17)-C(25)-C(26)	112.8(4)
C(4)-C(5)-C(6)	116.3(3)	C(17)-C(25)-C(27)	109.8(3)
C(4)-C(5)-C(13)	122.8(3)	C(26)-C(25)-C(27)	109.0(4)

Structural Data for L¹:As–As:L¹ **2** (L¹ = :C{N(2,6-*i*Pr₂C₆H₃)CH}₂).

Table 11. Crystal data and structure refinement for **2**.

Empirical formula	C ₅₄ H ₇₂ As ₂ N ₄
Formula weight	927.0
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.842(4) Å b = 11.160(4) Å c = 12.592(5) Å α= 95.640(5)° β = 112.601(5)° γ = 108.741(5)°
Volume	1288.6(9) Å ³
Z, Calculated density	1, 1.195 Mg/m ³
Absorption coefficient	1.334 mm ⁻¹
F(000)	490
Crystal size	0.20 x 0.18 x 0.08 mm
Theta range for data collection	2.15 to 28.28°
Limiting indices	-14<=h<=14, -14<=k<=14, -16<=l<=16
Reflections collected / unique	17857 / 6396 [R(int) = 0.0274]
Completeness to theta =	28.28 99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9008 and 0.7763
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6396 / 213 / 355
Goodness-of-fit on F ²	1.005
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.0804
R indices (all data)	R1 = 0.0572, wR2 = 0.0890
Largest diff. peak and hole	0.388 and -0.179 e.Å ⁻³

Table 12. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**.

Atom	X	Y	Z	U (eq)
As(1)	5696(1)	416(1)	1078(1)	50(1)
N(1)	6798(2)	3030(1)	2390(1)	40(1)
N(2)	5618(2)	3004(1)	549(1)	42(1)
C(1)	5996(2)	2196(2)	1264(1)	35(1)
C(2)	6892(3)	4290(2)	2360(2)	56(1)
C(3)	6174(3)	4277(2)	1234(2)	62(1)
C(4)	4756(2)	2624(2)	-712(2)	47(1)
C(5)	5455(3)	2794(3)	-1439(2)	70(1)
C(6)	4572(5)	2385(4)	-2657(3)	104(1)
C(7)	3122(5)	1874(4)	-3113(3)	110(1)
C(8)	2449(3)	1768(3)	-2398(3)	92(1)
C(9)	3250(3)	2142(2)	-1154(2)	65(1)
C(10)	2511(10)	2234(9)	-404(9)	76(2)
C(11)	2113(10)	1004(10)	-10(7)	94(2)
C(12)	1162(8)	2557(9)	-971(9)	125(3)
C(10')	2549(12)	1803(10)	-261(13)	78(3)
C(11')	1169(10)	594(9)	-734(12)	134(4)
C(12')	2324(13)	2997(8)	177(11)	125(4)
C(13)	7129(12)	3422(10)	-910(12)	86(3)
C(14)	7711(17)	4210(12)	-1682(9)	144(4)
C(15)	7761(9)	2392(8)	-687(15)	109(3)
C(13')	6910(40)	3280(30)	-1030(40)	110(8)
C(14')	7380(40)	4530(20)	-1470(30)	156(8)
C(15')	7500(30)	2310(20)	-1360(40)	117(6)
C(16)	7329(2)	2612(2)	3460(2)	44(1)
C(17)	8718(2)	2606(2)	3895(2)	57(1)
C(18)	9199(3)	2218(3)	4950(2)	82(1)
C(19)	8339(3)	1870(3)	5527(2)	90(1)
C(20)	6988(3)	1885(3)	5072(2)	73(1)
C(21)	6435(2)	2247(2)	4022(2)	51(1)
C(22)	4936(2)	2266(2)	3531(2)	61(1)
C(23)	3801(3)	1031(3)	3530(3)	98(1)
C(24)	4920(4)	3469(3)	4195(3)	94(1)
C(25)	9681(13)	2965(11)	3347(14)	73(3)
C(26)	11033(18)	4238(12)	3997(12)	108(4)
C(27)	10186(19)	1917(14)	2940(18)	134(5)
C(25')	9619(11)	3032(12)	3166(14)	66(3)
C(26')	10414(17)	4501(12)	3585(15)	103(4)
C(27')	10633(18)	2280(20)	3438(16)	117(5)

Table 13. Bond lengths [\AA] for **2**.

Atoms	Distance	Atoms	Distance
As(1)-C(1)	1.8809(18)	C(10')-C(11')	1.508(11)
As(1)-As(1)#1	2.4422(10)	C(10')-C(12')	1.518(11)
N(1)-C(1)	1.381(2)	C(13)-C(15)	1.514(8)
N(1)-C(2)	1.382(2)	C(13)-C(14)	1.549(8)
N(1)-C(16)	1.436(2)	C(13')-C(14')	1.554(16)
N(2)-C(1)	1.381(2)	C(13')-C(15')	1.528(13)
N(2)-C(3)	1.391(2)	C(16)-C(17)	1.394(3)
N(2)-C(4)	1.431(2)	C(16)-C(21)	1.392(3)
C(2)-C(3)	1.325(3)	C(17)-C(18)	1.397(3)
C(4)-C(5)	1.387(3)	C(17)-C(25)	1.437(13)
C(4)-C(9)	1.394(3)	C(17)-C(25')	1.580(12)
C(5)-C(6)	1.389(4)	C(18)-C(19)	1.374(4)
C(5)-C(13')	1.35(4)	C(19)-C(20)	1.360(4)
C(5)-C(13)	1.546(11)	C(20)-C(21)	1.386(3)
C(6)-C(7)	1.339(5)	C(21)-C(22)	1.509(3)
C(7)-C(8)	1.351(5)	C(22)-C(24)	1.520(4)
C(8)-C(9)	1.405(4)	C(22)-C(23)	1.524(4)
C(9)-C(10)	1.469(11)	C(25)-C(26)	1.533(10)
C(9)-C(10')	1.594(14)	C(25)-C(27)	1.562(10)
C(10)-C(11)	1.495(9)	C(25')-C(26')	1.511(11)
C(10)-C(12)	1.539(9)	C(25')-C(27')	1.545(10)

Table 14. Bond angles [°] for **2**.

Atoms	Angle	Atoms	Angle
C(1)-As(1)-As(1)#1	101.11(5)	C(11')-C(10')-C(12')	110.8(9)
C(1)-N(1)-C(2)	111.04(15)	C(11')-C(10')-C(9)	116.3(11)
C(1)-N(1)-C(16)	124.10(15)	C(12')-C(10')-C(9)	107.7(7)
C(2)-N(1)-C(16)	124.56(15)	C(5)-C(13)-C(15)	110.6(7)
C(1)-N(2)-C(3)	110.23(15)	C(5)-C(13)-C(14)	114.3(9)
C(1)-N(2)-C(4)	126.52(15)	C(15)-C(13)-C(14)	108.9(6)
C(3)-N(2)-C(4)	123.24(15)	C(5)-C(13')-C(14')	109(2)
N(2)-C(1)-N(1)	103.39(14)	C(5)-C(13')-C(15')	114(2)
N(2)-C(1)-As(1)	137.63(13)	C(14')-C(13')-C(15')	111.5(17)
N(1)-C(1)-As(1)	118.98(12)	C(17)-C(16)-C(21)	123.05(18)
C(3)-C(2)-N(1)	107.35(17)	C(17)-C(16)-N(1)	118.66(17)
C(2)-C(3)-N(2)	107.99(17)	C(21)-C(16)-N(1)	118.28(17)
C(5)-C(4)-C(9)	122.9(2)	C(16)-C(17)-C(18)	116.6(2)
C(5)-C(4)-N(2)	118.6(2)	C(16)-C(17)-C(25)	125.3(6)
C(9)-C(4)-N(2)	118.43(18)	C(18)-C(17)-C(25)	118.1(6)
C(4)-C(5)-C(6)	116.4(3)	C(16)-C(17)-C(25')	118.1(5)
C(4)-C(5)-C(13')	124.1(15)	C(18)-C(17)-C(25')	125.3(6)
C(6)-C(5)-C(13')	119.4(15)	C(25)-C(17)-C(25')	7.2(11)
C(4)-C(5)-C(13)	121.3(5)	C(17)-C(18)-C(19)	121.2(2)
C(6)-C(5)-C(13)	122.3(5)	C(20)-C(19)-C(18)	120.4(2)
C(13')-C(5)-C(13)	3.9(17)	C(19)-C(20)-C(21)	121.5(2)
C(7)-C(6)-C(5)	122.2(3)	C(20)-C(21)-C(16)	117.2(2)
C(6)-C(7)-C(8)	120.9(3)	C(20)-C(21)-C(22)	120.9(2)
C(7)-C(8)-C(9)	121.0(3)	C(16)-C(21)-C(22)	121.84(18)
C(4)-C(9)-C(8)	116.4(2)	C(21)-C(22)-C(24)	111.5(2)
C(4)-C(9)-C(10)	123.1(4)	C(21)-C(22)-C(23)	112.6(2)
C(8)-C(9)-C(10)	119.5(4)	C(24)-C(22)-C(23)	110.2(2)
C(4)-C(9)-C(10')	118.8(5)	C(17)-C(25)-C(26)	116.8(10)
C(8)-C(9)-C(10')	123.8(5)	C(17)-C(25)-C(27)	118.4(11)
C(10)-C(9)-C(10')	19.7(4)	C(26)-C(25)-C(27)	106.9(9)
C(9)-C(10)-C(11)	110.4(6)	C(26')-C(25')-C(17)	107.6(8)
C(9)-C(10)-C(12)	115.2(7)	C(26')-C(25')-C(27')	113.8(9)
C(11)-C(10)-C(12)	109.4(7)	C(17)-C(25')-C(27')	104.8(11)

Structural Data for $[L^1:\text{As}=\text{As}:L^1]^{+}[\text{GaCl}_4]^{-}$ **6** $^{+}[\text{GaCl}_4]^{-}$.

Table 15. Crystal data and structural refinement for **6** $^{+}[\text{GaCl}_4]^{-}$.

Empirical formula	C ₁₁₂ H ₁₅₂ As ₄ Cl ₈ Ga ₂ N ₈ O ₁
Formula weight	2349.14
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 24.040(8) Å b = 27.149(10) Å c = 22.396(8) Å α = 90° β = 121.465(4)° γ = 90°
Volume	12467(7) Å ³
Z, Calculated density	4, 1.252 Mg/m ³
Absorption coefficient	1.703 mm ⁻¹
F(000)	4872
Crystal size	0.35 x 0.30 x 0.14 mm
Theta range for data collection	2.26 to 25.00°
Limiting indices	-28<=h<=28, -32<=k<=32, -26<=l<=26
Reflections collected / unique	66181 / 10978 [R(int) = 0.0435]
Completeness to theta = 25.00	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7965 and 0.5871
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10978 / 2 / 700
Goodness-of-fit on F ²	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0549, wR2 = 0.1643
R indices (all data)	R1 = 0.0804, wR2 = 0.1872
Largest diff. peak and hole	0.556 and -1.436 e.Å ⁻³

Table 16. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $\mathbf{6}^+[\text{GaCl}_4]^-$.

Atom	X	Y	Z	U(eq)
As(1)	7890(1)	1257(1)	8441(1)	50(1)
As(1A)	7728(4)	1347(3)	8278(4)	85(3)
As(2)	7367(1)	899(1)	7331(1)	65(1)
As(2A)	7510(5)	748(3)	7457(5)	78(3)
N(1)	8358(2)	2201(1)	8222(2)	48(1)
N(2)	8894(2)	1599(1)	8123(2)	50(1)
N(3)	6595(2)	369(1)	7872(2)	46(1)
N(4)	6311(1)	217(1)	6800(2)	44(1)
C(1)	8391(2)	1702(1)	8207(2)	44(1)
C(2)	8845(2)	2404(2)	8144(3)	64(1)
C(3)	9175(2)	2032(2)	8080(3)	66(1)
C(4)	9163(2)	1112(2)	8166(3)	59(1)
C(5)	9025(2)	877(2)	7554(3)	68(1)
C(6)	9299(3)	401(2)	7641(4)	94(2)
C(7)	9676(4)	202(2)	8268(5)	108(2)
C(8)	9818(3)	443(2)	8860(4)	102(2)
C(9)	9570(3)	918(2)	8841(3)	74(1)
C(10)	9754(3)	1194(2)	9501(3)	88(2)
C(11)	10418(4)	1425(3)	9817(4)	125(3)
C(12)	9724(4)	882(3)	10045(4)	134(3)
C(13)	8623(3)	1104(2)	6839(3)	80(2)
C(14)	8158(4)	749(3)	6270(4)	124(3)
C(15)	9062(4)	1355(3)	6624(4)	107(2)
C(16)	7923(2)	2474(1)	8365(2)	52(1)
C(17)	7342(2)	2660(2)	7805(3)	62(1)
C(18)	6949(3)	2923(2)	7982(3)	80(2)
C(19)	7122(3)	2987(2)	8674(4)	83(2)
C(20)	7681(3)	2800(2)	9194(3)	75(1)
C(21)	8112(2)	2537(2)	9065(2)	60(1)
C(22)	8752(3)	2341(2)	9669(3)	69(1)
C(23)	9258(3)	2750(3)	10003(4)	121(3)
C(24)	8676(4)	2074(3)	10217(4)	113(2)
C(25)	7138(3)	2588(2)	7061(3)	86(2)
C(26)	7216(5)	3059(3)	6735(4)	153(4)
C(27)	6433(4)	2413(3)	6608(4)	143(3)
C(28)	6746(2)	472(1)	7380(2)	42(1)
C(29)	6067(2)	50(2)	7592(2)	59(1)
C(30)	5895(2)	-44(2)	6933(2)	57(1)
C(31)	6352(2)	165(2)	6185(2)	49(1)
C(32)	6015(2)	504(2)	5638(2)	63(1)
C(33)	6096(3)	442(2)	5060(3)	88(2)
C(34)	6471(3)	67(3)	5045(3)	99(2)
C(35)	6782(3)	-247(3)	5580(3)	88(2)

Table 16. (con't).

Atom	X	Y	Z	U(eq)
C(36)	6736(2)	-216(2)	6176(2)	63(1)
C(37)	7075(3)	-584(2)	6757(3)	80(2)
C(38)	6752(4)	-1089(3)	6520(5)	126(3)
C(39)	7797(3)	-624(3)	7041(5)	137(3)
C(40)	5591(3)	900(2)	5645(3)	89(2)
C(41)	4897(4)	783(3)	5184(5)	132(3)
C(42)	5736(5)	1397(3)	5408(7)	192(5)
C(43)	6966(2)	523(2)	8594(2)	50(1)
C(44)	6756(2)	935(2)	8798(2)	56(1)
C(45)	7150(3)	1076(2)	9497(3)	73(1)
C(46)	7703(3)	828(2)	9952(3)	80(2)
C(47)	7883(3)	418(2)	9743(3)	77(2)
C(48)	7519(2)	245(2)	9051(2)	61(1)
C(49)	7704(3)	-222(2)	8835(3)	80(2)
C(50)	8405(3)	-210(3)	8987(5)	133(3)
C(51)	7582(6)	-662(3)	9140(5)	157(4)
C(52)	6137(3)	1207(2)	8302(3)	70(1)
C(53)	6253(3)	1760(2)	8309(4)	113(2)
C(54)	5618(3)	1096(3)	8477(4)	126(3)
Ga(1)	10000	1337(4)	12500	111(7)
Ga(1A)	9902(4)	1310(2)	12593(5)	60(1)
Cl(1A)	10791(7)	888(5)	13356(7)	104(3)
Cl(1B)	10815(8)	923(7)	13093(14)	87(5)
Cl(1C)	10740(17)	997(14)	13220(30)	193(15)
Cl(2A)	10000	2072(5)	12500	169(12)
Cl(2B)	9893(12)	2003(6)	12797(14)	162(10)
Cl(3A)	9463(3)	1302(3)	13215(3)	117(2)
Cl(3B)	9680(13)	1679(18)	13197(12)	156(16)
Ga(2)	5000	1493(3)	2500	65(1)
Ga(2A)	4891(7)	1396(2)	2372(10)	148(3)
Cl(4A)	4581(4)	880(2)	1697(3)	139(2)
Cl(4B)	4032(11)	1093(7)	1515(8)	213(7)
Cl(4C)	5128(9)	1297(6)	1698(6)	163(7)
Cl(5)	4730(3)	2186(2)	2187(5)	198(4)
Cl(6A)	5632(16)	1356(4)	2023(17)	233(14)
Cl(6B)	6030(7)	1412(6)	2732(11)	189(7)
O(1)	7844	2611	5265	159
C(55)	7202	2633	4471	138
C(56)	7293	2230	5273	141
C(57)	7010	1885	4601	132
C(58)	6623	2320	4188	130

Table 17. Bond lengths [Å] for $\mathbf{6}^+[\text{GaCl}_4]^-$.

Atoms	Distance	Atoms	Distance
As(1)-C(1)	1.960(4)	C(31)-C(36)	1.393(6)
As(1)-As(2)	2.332(3)	C(31)-C(32)	1.401(6)
As(1A)-C(1)	1.939(10)	C(32)-C(33)	1.417(7)
As(1A)-As(2A)	2.301(12)	C(32)-C(40)	1.487(7)
As(2)-C(28)	1.938(5)	C(33)-C(34)	1.372(9)
As(2A)-C(28)	1.904(10)	C(34)-C(35)	1.337(9)
N(1)-C(1)	1.358(5)	C(35)-C(36)	1.396(7)
N(1)-C(2)	1.382(5)	C(36)-C(37)	1.502(7)
N(1)-C(16)	1.448(5)	C(37)-C(38)	1.528(9)
N(2)-C(1)	1.346(5)	C(37)-C(39)	1.509(8)
N(2)-C(3)	1.386(5)	C(40)-C(41)	1.467(9)
N(2)-C(4)	1.452(6)	C(40)-C(42)	1.555(12)
N(3)-C(28)	1.357(5)	C(43)-C(48)	1.402(6)
N(3)-C(29)	1.388(5)	C(43)-C(44)	1.398(6)
N(3)-C(43)	1.443(5)	C(44)-C(45)	1.394(7)
N(4)-C(28)	1.359(5)	C(44)-C(52)	1.507(7)
N(4)-C(30)	1.379(5)	C(45)-C(46)	1.360(8)
N(4)-C(31)	1.439(5)	C(46)-C(47)	1.364(8)
C(2)-C(3)	1.336(7)	C(47)-C(48)	1.404(7)
C(4)-C(5)	1.386(7)	C(48)-C(49)	1.505(7)
C(4)-C(9)	1.407(7)	C(49)-C(51)	1.478(9)
C(5)-C(6)	1.416(8)	C(49)-C(50)	1.537(9)
C(5)-C(13)	1.504(8)	C(52)-C(53)	1.526(8)
C(6)-C(7)	1.326(10)	C(52)-C(54)	1.518(8)
C(7)-C(8)	1.351(10)	Ga(1)-Cl(2A)	1.994(18)
C(8)-C(9)	1.413(8)	Ga(1)-Cl(2B)	1.99(2)
C(9)-C(10)	1.502(8)	Ga(1)-Cl(2B)#1	1.99(2)
C(10)-C(12)	1.517(9)	Ga(1)-Cl(1B)#1	2.037(19)
C(10)-C(11)	1.505(9)	Ga(1)-Cl(1B)	2.037(19)
C(13)-C(15)	1.532(8)	Ga(1)-Cl(1C)#1	1.91(3)
C(13)-C(14)	1.521(8)	Ga(1)-Cl(1C)	1.91(3)
C(16)-C(21)	1.395(6)	Ga(1)-Cl(1A)#1	2.230(14)
C(16)-C(17)	1.397(6)	Ga(1)-Cl(1A)	2.230(13)
C(17)-C(18)	1.397(7)	Ga(1)-Cl(3B)	2.27(2)
C(17)-C(25)	1.483(7)	Ga(1)-Cl(3B)#1	2.27(2)
C(18)-C(19)	1.389(8)	Ga(1A)-Cl(1B)#1	1.92(2)
C(19)-C(20)	1.338(8)	Ga(1A)-Cl(3B)	1.97(2)
C(20)-C(21)	1.406(7)	Ga(1A)-Cl(2B)	1.938(19)
C(21)-C(22)	1.519(7)	Ga(1A)-Cl(1C)	1.95(3)
C(22)-C(24)	1.516(8)	Ga(1A)-Cl(1C)#1	1.87(3)
C(22)-C(23)	1.522(8)	Ga(1A)-Cl(3A)	2.144(12)
C(25)-C(26)	1.533(9)	Ga(1A)-Cl(2A)	2.104(16)
C(25)-C(27)	1.529(9)	Ga(1A)-Cl(1B)	2.146(17)
C(29)-C(30)	1.333(6)	Ga(1A)-Cl(1A)#1	2.215(14)

Table 17. (cont'd).

Atoms	Distance	Atoms	Distance
Ga(1A)-Cl(1A)	2.233(15)	Ga(2A)-Cl(4B)	2.12(2)
Ga(1A)-Cl(2B)#1	2.23(2)	Ga(2A)-Cl(6B)#2	2.10(2)
Cl(1A)-Ga(1A)#1	2.215(14)	Ga(2A)-Cl(4C)#2	2.12(2)
Cl(1B)-Ga(1A)#1	1.92(2)	Ga(2A)-Cl(5)	2.178(9)
Cl(1C)-Ga(1A)#1	1.87(3)	Ga(2A)-Cl(4A)#2	2.271(17)
Cl(2A)-Ga(1A)#1	2.104(16)	Ga(2A)-Cl(6A)#2	2.28(2)
Cl(2B)-Ga(1A)#1	2.23(2)	Ga(2A)-Cl(6A)	2.29(2)
Ga(2)-Cl(5)#2	1.992(10)	Ga(2A)-Cl(5)#2	2.336(8)
Ga(2)-Cl(5)	1.992(10)	Ga(2A)-Cl(6B)	2.419(19)
Ga(2)-Cl(4C)	2.046(10)	Cl(4A)-Ga(2A)#2	2.271(17)
Ga(2)-Cl(4C)#2	2.046(10)	Cl(4C)-Ga(2A)#2	2.12(2)
Ga(2)-Cl(4A)	2.264(8)	Cl(5)-Ga(2A)#2	2.336(8)
Ga(2)-Cl(4A)#2	2.264(8)	Cl(6A)-Ga(2A)#2	2.28(2)
Ga(2)-Cl(6B)#2	2.260(13)	Cl(6B)-Ga(2A)#2	2.10(2)
Ga(2)-Cl(6B)	2.260(13)	O(1)-C(55)	1.6378(4)
Ga(2)-Cl(6A)#2	2.298(14)	O(1)-C(56)	1.6880(4)
Ga(2)-Cl(6A)	2.298(14)	C(55)-C(58)	1.4630(4)
Ga(2)-Cl(4B)	2.471(16)	C(56)-C(57)	1.5926(4)
Ga(2A)-Cl(4A)	1.905(13)	C(57)-C(58)	1.4890(4)
Ga(2A)-Cl(4C)	1.89(2)		

Table 18. Bond angles [°] for $\mathbf{6}^{\bullet+}[\text{GaCl}_4]^-$.

Atoms	Distance	Atoms	Distance
C(1)-As(1)-As(2)	92.10(14)	C(16)-C(17)-C(18)	115.9(5)
C(1)-As(1A)-As(2A)	98.1(5)	C(16)-C(17)-C(25)	123.4(4)
C(28)-As(2)-As(1)	101.02(16)	C(18)-C(17)-C(25)	120.7(5)
C(28)-As(2A)-As(1A)	99.0(5)	C(19)-C(18)-C(17)	121.9(5)
C(1)-N(1)-C(2)	109.3(3)	C(18)-C(19)-C(20)	120.1(5)
C(1)-N(1)-C(16)	125.0(3)	C(19)-C(20)-C(21)	121.9(5)
C(2)-N(1)-C(16)	125.4(3)	C(16)-C(21)-C(20)	116.7(5)
C(1)-N(2)-C(3)	109.8(3)	C(16)-C(21)-C(22)	122.8(4)
C(1)-N(2)-C(4)	125.7(3)	C(20)-C(21)-C(22)	120.4(5)
C(3)-N(2)-C(4)	124.1(3)	C(21)-C(22)-C(24)	113.2(5)
C(28)-N(3)-C(29)	109.4(3)	C(21)-C(22)-C(23)	111.2(5)
C(28)-N(3)-C(43)	125.4(3)	C(24)-C(22)-C(23)	110.7(5)
C(29)-N(3)-C(43)	124.8(3)	C(17)-C(25)-C(26)	112.1(5)
C(28)-N(4)-C(30)	109.8(3)	C(17)-C(25)-C(27)	112.8(6)
C(28)-N(4)-C(31)	124.2(3)	C(26)-C(25)-C(27)	108.2(6)
C(30)-N(4)-C(31)	125.3(3)	N(3)-C(28)-N(4)	105.8(3)
N(1)-C(1)-N(2)	106.2(3)	N(3)-C(28)-As(2)	135.3(3)
N(1)-C(1)-As(1)	123.9(3)	N(4)-C(28)-As(2)	118.9(3)
N(2)-C(1)-As(1)	129.0(3)	N(3)-C(28)-As(2A)	131.4(4)
N(1)-C(1)-As(1A)	115.7(4)	N(4)-C(28)-As(2A)	120.8(4)
N(2)-C(1)-As(1A)	138.0(4)	C(30)-C(29)-N(3)	107.5(4)
As(1)-C(1)-As(1A)	13.1(3)	C(29)-C(30)-N(4)	107.5(4)
C(3)-C(2)-N(1)	107.6(4)	C(36)-C(31)-C(32)	124.0(4)
C(2)-C(3)-N(2)	107.2(4)	C(36)-C(31)-N(4)	117.6(4)
C(5)-C(4)-C(9)	124.3(5)	C(32)-C(31)-N(4)	118.4(4)
C(5)-C(4)-N(2)	119.1(4)	C(31)-C(32)-C(33)	115.3(5)
C(9)-C(4)-N(2)	116.6(4)	C(31)-C(32)-C(40)	123.5(4)
C(4)-C(5)-C(6)	115.5(6)	C(33)-C(32)-C(40)	121.1(5)
C(4)-C(5)-C(13)	123.6(4)	C(32)-C(33)-C(34)	121.0(6)
C(6)-C(5)-C(13)	120.9(5)	C(35)-C(34)-C(33)	121.2(5)
C(7)-C(6)-C(5)	121.9(6)	C(34)-C(35)-C(36)	122.1(5)
C(6)-C(7)-C(8)	121.6(6)	C(35)-C(36)-C(31)	116.3(5)
C(7)-C(8)-C(9)	121.8(7)	C(35)-C(36)-C(37)	120.6(5)
C(4)-C(9)-C(8)	114.8(6)	C(31)-C(36)-C(37)	123.1(4)
C(4)-C(9)-C(10)	123.7(5)	C(36)-C(37)-C(38)	110.4(5)
C(8)-C(9)-C(10)	121.5(6)	C(36)-C(37)-C(39)	113.4(6)
C(9)-C(10)-C(12)	113.5(6)	C(38)-C(37)-C(39)	110.3(5)
C(9)-C(10)-C(11)	111.5(5)	C(41)-C(40)-C(32)	111.8(5)
C(12)-C(10)-C(11)	109.8(6)	C(41)-C(40)-C(42)	108.8(6)
C(5)-C(13)-C(15)	110.6(5)	C(32)-C(40)-C(42)	110.4(7)
C(5)-C(13)-C(14)	114.6(6)	C(48)-C(43)-C(44)	124.0(4)
C(15)-C(13)-C(14)	110.1(5)	C(48)-C(43)-N(3)	117.2(4)
C(21)-C(16)-C(17)	123.4(4)	C(44)-C(43)-N(3)	118.7(4)
C(21)-C(16)-N(1)	117.5(4)	C(43)-C(44)-C(45)	115.9(5)
C(17)-C(16)-N(1)	119.0(4)	C(43)-C(44)-C(52)	122.5(4)

Table 18 (con't).

Atoms	Distance	Atoms	Distance
C(45)-C(44)-C(52)	121.5(4)	Cl(1C)-Ga(1)-Cl(3B)	97(2)
C(46)-C(45)-C(44)	122.1(5)	Cl(1A)#1-Ga(1)-Cl(3B)	111.8(10)
C(45)-C(46)-C(47)	120.5(5)	Cl(1A)-Ga(1)-Cl(3B)	94.4(9)
C(46)-C(47)-C(48)	121.7(5)	Cl(2B)-Ga(1)-Cl(3B)#1	90.5(18)
C(43)-C(48)-C(47)	115.6(5)	Cl(1B)#1-Ga(1)-Cl(3B)#1	109.4(10)
C(43)-C(48)-C(49)	123.1(4)	Cl(1B)-Ga(1)-Cl(3B)#1	96.9(13)
C(47)-C(48)-C(49)	121.2(5)	Cl(1C)#1-Ga(1)-Cl(3B)#1	97(2)
C(51)-C(49)-C(48)	111.6(5)	Cl(1C)-Ga(1)-Cl(3B)#1	106(2)
C(51)-C(49)-C(50)	112.1(6)	Cl(1A)#1-Ga(1)-Cl(3B)#1	94.4(9)
C(48)-C(49)-C(50)	112.6(5)	Cl(1A)-Ga(1)-Cl(3B)#1	111.8(10)
C(44)-C(52)-C(53)	111.6(5)	Ga(1A)#1-Ga(1A)-Cl(1B)#1	96.5(15)
C(44)-C(52)-C(54)	110.0(5)	Ga(1A)#1-Ga(1A)-Cl(3B)	145.9(18)
C(53)-C(52)-C(54)	111.4(5)	Cl(1B)#1-Ga(1A)-Cl(3B)	112.2(14)
Ga(1A)#1-Ga(1)-Cl(1B)#1	101(2)	Ga(1A)#1-Ga(1A)-Cl(2B)	102.2(9)
Cl(2A)-Ga(1)-Cl(1B)#1	123.5(6)	Cl(1B)#1-Ga(1A)-Cl(2B)	127.3(10)
Cl(2B)-Ga(1)-Cl(1B)#1	118.2(10)	Cl(1B)#1-Ga(1A)-Cl(1C)	119.9(13)
Cl(2B)#1-Ga(1)-Cl(1B)#1	122.1(9)	Cl(3B)-Ga(1A)-Cl(1C)	106(2)
Cl(2A)-Ga(1)-Cl(1B)	123.5(6)	Cl(2B)-Ga(1A)-Cl(1C)	112.7(16)
Cl(2B)-Ga(1)-Cl(1B)	122.1(9)	Cl(3B)-Ga(1A)-Cl(1C)#1	121(2)
Cl(2B)#1-Ga(1)-Cl(1B)	118.2(10)	Cl(2B)-Ga(1A)-Cl(1C)#1	124.5(15)
Cl(1B)#1-Ga(1)-Cl(1B)	113.0(12)	Cl(1C)-Ga(1A)-Cl(1C)#1	122(2)
Cl(2A)-Ga(1)-Cl(1C)#1	119.0(13)	Cl(1C)-Ga(1A)-Cl(3A)	101(2)
Cl(2B)-Ga(1)-Cl(1C)#1	119.9(15)	Cl(1C)#1-Ga(1A)-Cl(3A)	101(2)
Cl(2B)#1-Ga(1)-Cl(1C)#1	112.4(17)	Cl(1B)#1-Ga(1A)-Cl(2A)	124.0(7)
Cl(1B)-Ga(1)-Cl(1C)#1	116.1(13)	Cl(1C)-Ga(1A)-Cl(2A)	111.9(12)
Cl(2A)-Ga(1)-Cl(1C)	119.0(13)	Cl(1C)#1-Ga(1A)-Cl(2A)	115.3(15)
Cl(2B)-Ga(1)-Cl(1C)	112.4(17)	Cl(3A)-Ga(1A)-Cl(2A)	101.1(4)
Cl(2B)#1-Ga(1)-Cl(1C)	119.9(15)	Cl(1B)#1-Ga(1A)-Cl(1B)	113.4(10)
Cl(1B)#1-Ga(1)-Cl(1C)	116.1(13)	Cl(3B)-Ga(1A)-Cl(1B)	117.4(10)
Cl(1C)#1-Ga(1)-Cl(1C)	122(3)	Cl(2B)-Ga(1A)-Cl(1B)	119.1(10)
Cl(2A)-Ga(1)-Cl(1A)#1	123.2(5)	Cl(1C)#1-Ga(1A)-Cl(1B)	112.6(14)
Cl(2B)-Ga(1)-Cl(1A)#1	125.7(8)	Cl(3A)-Ga(1A)-Cl(1B)	111.8(9)
Cl(2B)#1-Ga(1)-Cl(1A)#1	114.3(9)	Cl(2A)-Ga(1A)-Cl(1B)	113.3(7)
Cl(1B)-Ga(1)-Cl(1A)#1	110.9(7)	Cl(3B)-Ga(1A)-Cl(1A)#1	125.8(11)
Cl(1C)-Ga(1)-Cl(1A)#1	117.7(12)	Cl(2B)-Ga(1A)-Cl(1A)#1	129.3(9)
Cl(2A)-Ga(1)-Cl(1A)	123.2(5)	Cl(1C)-Ga(1A)-Cl(1A)#1	116.4(13)
Cl(2B)-Ga(1)-Cl(1A)	114.3(9)	Cl(3A)-Ga(1A)-Cl(1A)#1	103.8(6)
Cl(2B)#1-Ga(1)-Cl(1A)	125.7(8)	Cl(2A)-Ga(1A)-Cl(1A)#1	118.7(6)
Cl(1B)#1-Ga(1)-Cl(1A)	110.9(7)	Cl(1B)-Ga(1A)-Cl(1A)#1	107.4(6)
Cl(1C)#1-Ga(1)-Cl(1A)	117.7(12)	Cl(1B)#1-Ga(1A)-Cl(1A)	115.7(6)
Cl(1A)#1-Ga(1)-Cl(1A)	113.6(9)	Cl(3B)-Ga(1A)-Cl(1A)	103.3(9)
Cl(2B)#1-Ga(1)-Cl(3B)	90.5(18)	Cl(2B)-Ga(1A)-Cl(1A)	116.2(9)
Cl(1B)#1-Ga(1)-Cl(3B)	96.9(13)	Cl(1C)#1-Ga(1A)-Cl(1A)	119.1(11)
Cl(1B)-Ga(1)-Cl(3B)	109.4(10)	Cl(3A)-Ga(1A)-Cl(1A)	95.6(6)
Cl(1C)#1-Ga(1)-Cl(3B)	106(2)	Cl(2A)-Ga(1A)-Cl(1A)	117.9(5)

Table 18 (con't).

Atoms	Distance	Atoms	Distance
Cl(1A)#1-Ga(1A)-Cl(1A)	114.1(8)	Cl(4A)-Ga(2A)-Cl(6B)#2	88.5(7)
Cl(1B)#1-Ga(1A)-Cl(2B)#1	115.9(10)	Cl(4C)-Ga(2A)-Cl(6B)#2	130.8(11)
Cl(1C)-Ga(1A)-Cl(2B)#1	107.2(16)	Cl(4A)-Ga(2A)-Cl(4C)#2	119.0(7)
Cl(1C)#1-Ga(1A)-Cl(2B)#1	103.7(19)	Cl(4B)-Ga(2A)-Cl(4C)#2	109.2(8)
Cl(3A)-Ga(1A)-Cl(2B)#1	123.2(7)	Cl(4A)-Ga(2A)-Cl(5)	128.1(10)
Cl(1B)-Ga(1A)-Cl(2B)#1	104.0(10)	Cl(4C)-Ga(2A)-Cl(5)	94.9(9)
Cl(1A)#1-Ga(1A)-Cl(2B)#1	105.6(9)	Cl(4B)-Ga(2A)-Cl(5)	102.6(9)
Cl(1A)-Ga(1A)-Cl(2B)#1	114.4(8)	Cl(6B)#2-Ga(2A)-Cl(5)	83.5(6)
Cl(5)#2-Ga(2)-Cl(4C)	112.5(7)	Cl(4C)#2-Ga(2A)-Cl(5)	102.6(8)
Cl(5)-Ga(2)-Cl(4C)	96.2(5)	Cl(4A)-Ga(2A)-Cl(4A)#2	94.2(5)
Cl(5)#2-Ga(2)-Cl(4C)#2	96.2(5)	Cl(4C)-Ga(2A)-Cl(4A)#2	112.8(7)
Cl(5)-Ga(2)-Cl(4C)#2	112.5(7)	Cl(4B)-Ga(2A)-Cl(4A)#2	113.9(6)
Cl(5)#2-Ga(2)-Cl(4A)	154.3(4)	Cl(6B)#2-Ga(2A)-Cl(4A)#2	99.6(9)
Cl(5)-Ga(2)-Cl(4A)	119.1(3)	Cl(5)-Ga(2A)-Cl(4A)#2	137.8(8)
Cl(4C)#2-Ga(2)-Cl(4A)	107.3(5)	Cl(4A)-Ga(2A)-Cl(6A)#2	109.1(8)
Cl(5)#2-Ga(2)-Cl(4A)#2	119.1(3)	Cl(4B)-Ga(2A)-Cl(6A)#2	86.6(10)
Cl(5)-Ga(2)-Cl(4A)#2	154.3(4)	Cl(5)-Ga(2A)-Cl(6A)#2	93.5(6)
Cl(4C)-Ga(2)-Cl(4A)#2	107.3(5)	Cl(4B)-Ga(2A)-Cl(6A)	103.7(12)
Ga(2A)#2-Ga(2)-Cl(6B)#2	111(2)	Cl(4C)#2-Ga(2A)-Cl(6A)	138.3(10)
Cl(5)#2-Ga(2)-Cl(6B)#2	106.9(5)	Cl(5)-Ga(2A)-Cl(6A)	94.3(6)
Cl(5)-Ga(2)-Cl(6B)#2	84.0(5)	Cl(4A)#2-Ga(2A)-Cl(6A)	97.0(8)
Cl(4C)-Ga(2)-Cl(6B)#2	115.0(6)	Cl(4C)-Ga(2A)-Cl(5)#2	104.7(9)
Cl(4A)#2-Ga(2)-Cl(6B)#2	95.2(5)	Cl(4B)-Ga(2A)-Cl(5)#2	136.1(9)
Cl(5)#2-Ga(2)-Cl(6B)	84.0(5)	Cl(6B)#2-Ga(2A)-Cl(5)#2	100.7(6)
Cl(5)-Ga(2)-Cl(6B)	106.9(5)	Cl(4A)#2-Ga(2A)-Cl(5)#2	105.7(7)
Cl(4C)#2-Ga(2)-Cl(6B)	115.0(6)	Cl(6A)#2-Ga(2A)-Cl(5)#2	90.4(7)
Cl(4A)-Ga(2)-Cl(6B)	95.2(5)	Cl(6A)-Ga(2A)-Cl(5)#2	89.2(7)
Cl(5)#2-Ga(2)-Cl(6A)#2	99.4(5)	Cl(4A)-Ga(2A)-Cl(6B)	100.5(8)
Cl(5)-Ga(2)-Cl(6A)#2	98.2(5)	Cl(4C)#2-Ga(2A)-Cl(6B)	106.0(9)
Cl(4C)-Ga(2)-Cl(6A)#2	143.7(7)	Cl(5)-Ga(2A)-Cl(6B)	96.0(5)
Cl(4A)-Ga(2)-Cl(6A)#2	97.0(6)	C(55)-O(1)-C(56)	74.57(2)
Cl(5)#2-Ga(2)-Cl(6A)	98.2(5)	C(58)-C(55)-O(1)	126.397(13)
Cl(5)-Ga(2)-Cl(6A)	99.4(5)	C(58)-C(55)-C(56)	72.952(15)
Cl(4A)#2-Ga(2)-Cl(6A)	97.0(6)	O(1)-C(55)-C(56)	53.85(2)
Cl(5)#2-Ga(2)-Cl(4B)	135.3(6)	C(57)-C(56)-O(1)	107.508(17)
Cl(5)-Ga(2)-Cl(4B)	96.8(5)	C(57)-C(56)-C(55)	71.51(3)
Cl(4C)#2-Ga(2)-Cl(4B)	99.6(5)	O(1)-C(56)-C(55)	51.576(9)
Cl(4A)#2-Ga(2)-Cl(4B)	101.9(5)	C(58)-C(57)-C(56)	86.61(2)
Cl(6B)-Ga(2)-Cl(4B)	124.8(7)	C(55)-C(58)-C(57)	92.69(2)
Cl(6A)-Ga(2)-Cl(4B)	93.3(9)		

Structural Data for $[L^1:As=As:L^1]^{2+}[GaCl_4]^-_2 \text{ } \mathbf{6}^{2+}[GaCl_4^-]_2$.

Table 19. Crystal data and structural refinement for $\mathbf{6}^{2+}[GaCl_4^-]_2$.

Empirical formula	$C_{58} H_{78} As Cl_8 Ga_2 N_6$
Formula weight	1432.14
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	$a = 15.2173(10)$ Å $b = 18.3240(12)$ Å $c = 13.9424(9)$ Å $\alpha = 90^\circ$ $\beta = 115.9530(10)^\circ$ $\gamma = 90^\circ$
Volume	$3495.7(4)$ Å ³
Z, Calculated density	2, 1.361 Mg/m ³
Absorption coefficient	2.054 mm ⁻¹
F(000)	1464
Crystal size	0.40 x 0.35 x 0.14 mm
Theta range for data collection	2.22 to 27.00°
Limiting indices	-19<=h<=19, -23<=k<=23, -17<=l<=17
Reflections collected / unique	43129 / 7634 [R(int) = 0.0348]
Completeness to theta =	27.00 99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7619 and 0.4938
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7634 / 0 / 344
Goodness-of-fit on F ²	1.011
Final R indices [I>2sigma(I)]	R1 = 0.0385, wR2 = 0.0950
R indices (all data)	R1 = 0.0534, wR2 = 0.1045
Largest diff. peak and hole	0.921 and -0.657 e.Å ⁻³

Table 20. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $\mathbf{6}^{2+}[\text{GaCl}_4^-]_2$.

Atom	X	Y	Z	U(eq)
As(1)	4282(1)	4751(1)	4401(1)	42(1)
N(1)	3422(2)	5784(1)	5527(2)	38(1)
N(2)	2383(1)	5165(1)	4202(2)	35(1)
C(1)	3350(2)	5290(1)	4775(2)	33(1)
C(2)	2506(2)	5960(2)	5421(2)	46(1)
C(3)	1859(2)	5569(2)	4597(2)	44(1)
C(4)	1965(2)	4666(2)	3300(2)	39(1)
C(5)	1698(2)	4952(2)	2281(2)	46(1)
C(6)	1361(2)	4449(2)	1447(2)	64(1)
C(7)	1284(3)	3725(2)	1622(3)	71(1)
C(8)	1512(2)	3471(2)	2624(3)	64(1)
C(9)	1849(2)	3939(2)	3506(2)	48(1)
C(10)	2035(2)	3654(2)	4597(3)	58(1)
C(11)	1097(3)	3365(3)	4601(4)	98(1)
C(12)	2831(4)	3084(3)	4986(5)	125(2)
C(13)	1769(2)	5760(2)	2073(2)	56(1)
C(14)	2714(3)	5928(3)	1989(4)	88(1)
C(15)	900(3)	6029(3)	1069(3)	86(1)
C(16)	4328(2)	6101(1)	6299(2)	41(1)
C(17)	4672(2)	6724(2)	5995(2)	51(1)
C(18)	5582(2)	6979(2)	6725(3)	68(1)
C(19)	6092(2)	6637(2)	7685(3)	73(1)
C(20)	5710(2)	6052(2)	7978(3)	66(1)
C(21)	4797(2)	5759(2)	7293(2)	50(1)
C(22)	4337(2)	5149(2)	7645(2)	58(1)
C(23)	4025(4)	5436(3)	8475(4)	108(2)
C(24)	4988(4)	4485(3)	8058(5)	111(2)
C(25)	4067(2)	7140(2)	4981(3)	63(1)
C(26)	3659(4)	7828(2)	5259(5)	117(2)
C(27)	4604(4)	7323(3)	4311(4)	107(2)
Ga(1)	11482(1)	4094(1)	7664(1)	66(1)
Cl(1)	11025(1)	4972(1)	6522(1)	102(1)
Cl(2)	12683(1)	3501(1)	7606(1)	106(1)
Cl(3)	10243(1)	3362(1)	7204(1)	115(1)
Cl(4)	11944(1)	4527(1)	9244(1)	149(1)
C(28)	11134(4)	6600(3)	8211(5)	122(2)
C(29)	11623(4)	6865(3)	7598(5)	100(2)
N(3)	12007(4)	7056(3)	7115(5)	129(2)

Table 21. Bond lengths [Å] for $\mathbf{6}^{2+}[\text{GaCl}_4^-]_2$.

Atoms	Distance	Atoms	Distance
As(1)-C(1)	1.977(2)	C(13)-C(15)	1.527(4)
As(1)-As(1)#1	2.2803(5)	C(16)-C(21)	1.399(4)
N(1)-C(1)	1.353(3)	C(16)-C(17)	1.396(4)
N(1)-C(2)	1.374(3)	C(17)-C(18)	1.393(4)
N(1)-C(16)	1.449(3)	C(17)-C(25)	1.512(5)
N(2)-C(1)	1.351(3)	C(18)-C(19)	1.370(6)
N(2)-C(3)	1.369(3)	C(19)-C(20)	1.364(6)
N(2)-C(4)	1.456(3)	C(20)-C(21)	1.403(4)
C(2)-C(3)	1.348(4)	C(21)-C(22)	1.510(5)
C(4)-C(9)	1.390(4)	C(22)-C(23)	1.524(5)
C(4)-C(5)	1.399(4)	C(22)-C(24)	1.514(5)
C(5)-C(6)	1.394(4)	C(25)-C(26)	1.528(5)
C(5)-C(13)	1.521(5)	C(25)-C(27)	1.524(6)
C(6)-C(7)	1.364(5)	Ga(1)-Cl(4)	2.1496(15)
C(7)-C(8)	1.366(5)	Ga(1)-Cl(1)	2.1530(11)
C(8)-C(9)	1.399(4)	Ga(1)-Cl(2)	2.1588(11)
C(9)-C(10)	1.514(4)	Ga(1)-Cl(3)	2.1689(13)
C(10)-C(12)	1.509(5)	C(28)-C(29)	1.440(8)
C(10)-C(11)	1.525(5)	C(29)-N(3)	1.125(7)
C(13)-C(14)	1.523(5)		

Table 22. Bond angles [°] for $\mathbf{6}^{2+}[\text{GaCl}_4^-]_2$.

Atoms	Angle	Atoms	Angle
C(1)-As(1)-As(1)#1	100.10(7)	C(5)-C(13)-C(14)	111.0(3)
C(1)-N(1)-C(2)	109.9(2)	C(5)-C(13)-C(15)	112.5(3)
C(1)-N(1)-C(16)	124.9(2)	C(14)-C(13)-C(15)	109.4(3)
C(2)-N(1)-C(16)	125.2(2)	C(21)-C(16)-C(17)	124.8(2)
C(1)-N(2)-C(3)	110.2(2)	C(21)-C(16)-N(1)	117.6(2)
C(1)-N(2)-C(4)	124.7(2)	C(17)-C(16)-N(1)	117.6(2)
C(3)-N(2)-C(4)	125.1(2)	C(16)-C(17)-C(18)	115.9(3)
N(2)-C(1)-N(1)	105.7(2)	C(16)-C(17)-C(25)	122.7(3)
N(2)-C(1)-As(1)	118.70(17)	C(18)-C(17)-C(25)	121.2(3)
N(1)-C(1)-As(1)	135.61(17)	C(19)-C(18)-C(17)	121.2(3)
C(3)-C(2)-N(1)	107.1(2)	C(18)-C(19)-C(20)	121.2(3)
C(2)-C(3)-N(2)	107.1(2)	C(19)-C(20)-C(21)	121.5(3)
C(9)-C(4)-C(5)	124.2(2)	C(16)-C(21)-C(20)	115.2(3)
C(9)-C(4)-N(2)	118.1(2)	C(16)-C(21)-C(22)	123.1(3)
C(5)-C(4)-N(2)	117.7(2)	C(20)-C(21)-C(22)	121.6(3)
C(6)-C(5)-C(4)	115.9(3)	C(21)-C(22)-C(23)	109.5(3)
C(6)-C(5)-C(13)	121.0(3)	C(21)-C(22)-C(24)	113.6(3)
C(4)-C(5)-C(13)	123.0(2)	C(23)-C(22)-C(24)	111.0(4)
C(7)-C(6)-C(5)	121.5(3)	C(17)-C(25)-C(26)	109.1(3)
C(8)-C(7)-C(6)	120.8(3)	C(17)-C(25)-C(27)	114.4(3)
C(7)-C(8)-C(9)	121.4(3)	C(26)-C(25)-C(27)	111.1(4)
C(4)-C(9)-C(8)	115.9(3)	Cl(4)-Ga(1)-Cl(1)	109.72(7)
C(4)-C(9)-C(10)	123.6(3)	Cl(4)-Ga(1)-Cl(2)	108.74(7)
C(8)-C(9)-C(10)	120.4(3)	Cl(1)-Ga(1)-Cl(2)	110.68(6)
C(9)-C(10)-C(12)	111.6(3)	Cl(4)-Ga(1)-Cl(3)	112.57(7)
C(9)-C(10)-C(11)	111.1(3)	Cl(1)-Ga(1)-Cl(3)	106.61(6)
C(12)-C(10)-C(11)	111.3(4)	Cl(2)-Ga(1)-Cl(3)	108.52(5)
		N(3)-C(29)-C(28)	178.5(6)

Structural Data for compound containing a parent silylene (:SiH₂) unit **8**.

Table 23. Crystal data and structural refinement for **8**.

Empirical formula	C ₁₂₀ H ₁₉₂ B ₈ N ₈ O ₃ Si ₄
Formula weight	1993.66
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 13.9722(16) Å b = 22.691(3) Å c = 21.080(2) Å α= 90° β = 95.694(2)° γ = 90°
Volume	6650.3(13) Å ³
Z, Calculated density	2, 0.996 Mg/m ³
Absorption coefficient	0.092 mm ⁻¹
F(000)	2176
Crystal size	0.27 x 0.24 x 0.10 mm
Theta range for data collection	2.04 to 25.46°
Limiting indices	-16<=h<=16, -27<=k<=27, -25<=l<=25
Reflections collected / unique	72745 / 12260 [R(int) = 0.1169]
Completeness to theta =	25.46 99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9909 and 0.9757
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	12260 / 310 / 833
Goodness-of-fit on F ²	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0871, wR2 = 0.2098
R indices (all data)	R1 = 0.1967, wR2 = 0.2604
Largest diff. peak and hole	0.400 and -0.266 e.Å ⁻³

Table 24. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **8**.

Atom	X	Y	Z	U (eq)
Si(1)	9792(1)	257(1)	7261(1)	72(1)
Si(2)	8274(1)	1310(1)	7233(1)	91(1)
B(1)	9596(5)	1103(3)	7468(4)	73(2)
B(1')	9502(13)	1082(7)	7030(12)	78(7)
B(2)	9141(4)	-382(3)	7677(4)	114(2)
B(3)	7967(5)	-341(3)	7295(4)	102(2)
B(4)	8086(6)	-288(4)	8100(5)	139(3)
N(1)	11753(2)	-30(2)	6929(2)	69(1)
N(2)	11769(2)	119(2)	7934(2)	70(1)
N(3)	8134(3)	2589(2)	6944(2)	80(1)
N(4)	7353(2)	2367(1)	7729(2)	71(1)
C(1)	11167(3)	106(2)	7386(2)	63(1)
C(2)	12685(3)	-97(2)	7193(2)	91(2)
C(3)	12696(3)	-10(2)	7817(2)	87(1)
C(4)	11521(3)	198(2)	8580(2)	75(1)
C(5)	11302(3)	-301(3)	8923(2)	87(1)
C(6)	11148(4)	-221(3)	9550(3)	119(2)
C(7)	11205(5)	320(4)	9830(3)	137(2)
C(8)	11416(4)	806(3)	9484(3)	127(2)
C(9)	11590(3)	759(3)	8845(2)	91(1)
C(10)	11895(4)	1289(3)	8487(3)	108(2)
C(11)	12967(5)	1394(4)	8624(4)	185(3)
C(12)	11375(5)	1861(3)	8636(3)	156(3)
C(13)	11274(4)	-912(3)	8646(3)	112(2)
C(14)	10441(5)	-1292(3)	8857(3)	150(2)
C(15)	12239(5)	-1224(3)	8815(4)	179(3)
C(16)	11491(3)	-127(2)	6256(2)	74(1)
C(17)	11644(3)	322(3)	5834(2)	92(1)
C(18)	11492(4)	196(3)	5178(3)	113(2)
C(19)	11201(4)	-343(4)	4980(3)	118(2)
C(20)	11040(4)	-780(3)	5399(3)	105(2)
C(21)	11180(3)	-688(2)	6062(2)	83(1)
C(22)	10983(4)	-1181(2)	6517(2)	99(2)
C(23)	10050(5)	-1514(3)	6322(3)	145(2)
C(24)	11843(5)	-1600(3)	6609(3)	154(3)
C(25)	11956(5)	929(3)	6053(3)	120(2)
C(26)	11289(5)	1407(3)	5763(3)	157(3)
C(27)	12995(5)	1060(4)	5896(4)	185(3)
C(28)	7914(3)	2129(2)	7304(2)	66(1)
C(29)	7700(4)	3097(2)	7136(3)	106(2)
C(30)	7221(4)	2956(2)	7623(2)	91(1)
C(31)	6879(4)	2050(2)	8209(3)	88(1)
C(32)	7296(5)	2057(3)	8833(3)	126(2)
C(33)	6774(7)	1778(4)	9280(4)	193(4)

Table 24. (con't).

Atom	X	Y	Z	U (eq)
C(34)	5864(10)	1532(5)	9062(8)	235(8)
C(35)	5562(9)	1503(6)	8463(6)	225(7)
C(36)	6009(5)	1790(3)	8009(4)	131(2)
C(37)	5680(30)	1853(18)	7290(11)	196(12)
C(38)	4830(40)	2280(20)	7340(30)	167(13)
C(39)	5363(19)	1380(20)	6780(30)	182(13)
C(37')	5539(14)	1760(7)	7350(7)	146(5)
C(38')	4660(20)	2159(12)	7173(15)	165(7)
C(39')	5234(11)	1103(9)	7240(19)	187(10)
C(40)	8352(14)	2198(15)	9007(13)	163(9)
C(41)	8220(30)	2654(18)	9537(16)	218(11)
C(42)	8891(17)	1661(18)	9312(9)	181(11)
C(40')	8157(14)	2460(11)	9023(9)	131(7)
C(41')	8010(30)	3023(18)	9397(18)	232(13)
C(42')	9013(17)	2110(20)	9309(13)	223(12)
C(43)	8630(5)	2567(2)	6372(2)	90(1)
C(44)	9579(5)	2744(3)	6405(3)	125(2)
C(45)	9987(6)	2777(3)	5839(4)	155(3)
C(46)	9494(7)	2627(3)	5282(4)	141(3)
C(47)	8571(6)	2441(3)	5260(3)	130(2)
C(48)	8099(5)	2409(2)	5810(3)	100(2)
C(49)	7051(5)	2226(3)	5787(3)	134(2)
C(50)	6380(6)	2760(5)	5598(4)	238(5)
C(51)	6808(6)	1730(5)	5327(5)	259(6)
C(52)	10278(10)	2801(10)	7032(7)	116(6)
C(53)	10357(16)	3450(11)	7228(12)	165(8)
C(54)	11305(11)	2521(11)	7086(10)	130(6)
C(52')	9906(18)	3116(10)	6990(9)	141(7)
C(53')	10010(20)	3779(10)	6908(14)	184(9)
C(54')	10910(20)	2835(13)	7084(15)	175(9)
O(1)	5532(14)	498(13)	3552(10)	203(10)
C(55)	4599(17)	436(12)	3461(9)	200(10)
C(56)	4261(15)	347(15)	4120(9)	231(11)
C(57)	4974(14)	661(19)	4544(10)	278(16)
C(58)	5821(13)	708(15)	4155(12)	295(19)
O(1')	5520(20)	266(18)	3740(20)	207(14)
C(55')	4580(20)	280(13)	3622(17)	191(13)
C(56')	4213(18)	869(14)	3852(17)	218(14)
C(57')	5090(20)	1164(13)	4120(20)	240(15)
C(58')	5770(20)	648(16)	4225(19)	239(16)
O(2)	10377(18)	4747(12)	5426(12)	416(13)
C(59)	10179(13)	4832(8)	6070(8)	193(7)
C(60)	9210(20)	4853(12)	6232(12)	302(12)
C(61)	8980(20)	4502(13)	5604(13)	315(13)
C(62)	9340(20)	4753(14)	5113(11)	334(15)

Table 25. Bond Distances [Å] for **8**.

Atoms	Distance	Atoms	Distance
Si(1)-C(1)	1.944(4)	C(6)-C(7)	1.360(8)
Si(1)-B(1')	1.966(17)	C(6)-H(6)	0.9300
Si(1)-B(2)	1.965(7)	C(7)-C(8)	1.371(8)
Si(1)-B(1)	1.994(8)	C(7)-H(7)	0.9300
Si(1)-H(1D)	1.49(4)	C(8)-C(9)	1.397(7)
Si(2)-B(1')	1.882(16)	C(8)-H(8)	0.9300
Si(2)-B(1)	1.922(7)	C(9)-C(10)	1.504(7)
Si(2)-C(28)	1.934(4)	C(10)-C(11)	1.516(8)
Si(2)-H(4D)	1.49(2)	C(10)-C(12)	1.537(8)
Si(2)-H(5D)	1.42(4)	C(10)-H(10)	0.9800
B(1)-H(2D)	1.145(19)	C(11)-H(11A)	0.9600
B(1)-H(3D)	1.119(19)	C(11)-H(11B)	0.9600
B(1')-H(3D)	1.155(19)	C(11)-H(11C)	0.9600
B(1')-H(2D')	1.15(2)	C(12)-H(12A)	0.9600
B(2)-B(3)	1.756(9)	C(12)-H(12B)	0.9600
B(2)-B(4)	1.811(11)	C(12)-H(12C)	0.9600
B(2)-H(6D)	1.278(19)	C(13)-C(15)	1.535(7)
B(2)-H(7D)	1.32(2)	C(13)-C(14)	1.549(7)
B(3)-B(4)	1.693(12)	C(13)-H(13)	0.9800
B(3)-H(8D)	1.383(19)	C(14)-H(14A)	0.9600
B(3)-H(9D)	1.12(5)	C(14)-H(14B)	0.9600
B(3)-H(10D)	1.09(7)	C(14)-H(14C)	0.9600
B(4)-H(10D)	1.59(2)	C(15)-H(15A)	0.9600
B(4)-H(11D)	1.31(2)	C(15)-H(15B)	0.9600
B(4)-H(12D)	1.26(2)	C(15)-H(15C)	0.9600
N(1)-C(1)	1.359(4)	C(16)-C(17)	1.384(6)
N(1)-C(2)	1.373(5)	C(16)-C(21)	1.392(6)
N(1)-C(16)	1.446(5)	C(17)-C(18)	1.407(7)
N(2)-C(1)	1.360(5)	C(17)-C(25)	1.504(7)
N(2)-C(3)	1.374(5)	C(18)-C(19)	1.343(8)
N(2)-C(4)	1.449(5)	C(18)-H(18)	0.9300
N(3)-C(28)	1.345(5)	C(19)-C(20)	1.362(8)
N(3)-C(29)	1.381(5)	C(19)-H(19)	0.9300
N(3)-C(43)	1.449(6)	C(20)-C(21)	1.406(6)
N(4)-C(28)	1.359(5)	C(20)-H(20)	0.9300
N(4)-C(30)	1.365(5)	C(21)-C(22)	1.518(7)
N(4)-C(31)	1.453(6)	C(22)-C(24)	1.530(7)
C(2)-C(3)	1.328(5)	C(22)-C(23)	1.527(7)
C(2)-H(2)	0.9300	C(22)-H(22)	0.9800
C(3)-H(3)	0.9300	C(23)-H(23A)	0.9600
C(4)-C(9)	1.388(6)	C(23)-H(23B)	0.9600
C(4)-C(5)	1.395(6)	C(23)-H(23C)	0.9600
C(5)-C(6)	1.373(7)	C(24)-H(24A)	0.9600
C(5)-C(13)	1.502(7)	C(24)-H(24B)	0.9600

Table 25 (con't).

Atoms	Distance	Atoms	Distance
C(24)-H(24C)	0.9600	C(40)-C(42)	1.539(14)
C(25)-C(26)	1.518(8)	C(40)-C(41)	1.545(19)
C(25)-C(27)	1.549(8)	C(40)-H(40)	0.9800
C(25)-H(25)	0.9800	C(41)-H(41A)	0.9600
C(26)-H(26A)	0.9600	C(41)-H(41B)	0.9600
C(26)-H(26B)	0.9600	C(41)-H(41C)	0.9600
C(26)-H(26C)	0.9600	C(42)-H(42A)	0.9600
C(27)-H(27A)	0.9600	C(42)-H(42B)	0.9600
C(27)-H(27B)	0.9600	C(42)-H(42C)	0.9600
C(27)-H(27C)	0.9600	C(40')-C(42')	1.516(16)
C(29)-C(30)	1.320(6)	C(40')-C(41')	1.525(17)
C(29)-H(29)	0.9300	C(40')-H(40')	0.9800
C(30)-H(30)	0.9300	C(41')-H(41D)	0.9600
C(31)-C(36)	1.379(8)	C(41')-H(41E)	0.9600
C(31)-C(32)	1.385(7)	C(41')-H(41F)	0.9600
C(32)-C(33)	1.398(9)	C(42')-H(42D)	0.9600
C(32)-C(40)	1.519(17)	C(42')-H(42E)	0.9600
C(32)-C(40')	1.533(15)	C(42')-H(42F)	0.9600
C(33)-C(34)	1.422(15)	C(43)-C(44)	1.380(7)
C(33)-H(33)	0.9300	C(43)-C(48)	1.381(7)
C(34)-C(35)	1.293(17)	C(44)-C(45)	1.375(8)
C(34)-H(34)	0.9300	C(44)-C(52')	1.528(15)
C(35)-C(36)	1.361(11)	C(44)-C(52)	1.570(12)
C(35)-H(35)	0.9300	C(45)-C(46)	1.345(9)
C(36)-C(37')	1.477(12)	C(45)-H(45)	0.9300
C(36)-C(37)	1.547(19)	C(46)-C(47)	1.353(9)
C(37)-C(38)	1.542(19)	C(46)-H(46)	0.9300
C(37)-C(39)	1.560(14)	C(47)-C(48)	1.391(8)
C(37)-H(37)	0.9800	C(47)-H(47)	0.9300
C(38)-H(38A)	0.9600	C(48)-C(49)	1.519(8)
C(38)-H(38B)	0.9600	C(49)-C(51)	1.503(9)
C(38)-H(38C)	0.9600	C(49)-C(50)	1.558(9)
C(39)-H(39A)	0.9600	C(49)-H(49)	0.9800
C(39)-H(39B)	0.9600	C(50)-H(50A)	0.9600
C(39)-H(39C)	0.9600	C(50)-H(50B)	0.9600
C(37')-C(38')	1.544(12)	C(50)-H(50C)	0.9600
C(37')-C(39')	1.560(11)	C(51)-H(51A)	0.9600
C(37')-H(37')	0.9800	C(51)-H(51B)	0.9600
C(38')-H(38D)	0.9600	C(51)-H(51C)	0.9600
C(38')-H(38E)	0.9600	C(52)-C(53)	1.529(12)
C(38')-H(38F)	0.9600	C(52)-C(54)	1.564(13)
C(39')-H(39D)	0.9600	C(52)-H(52)	0.9800
C(39')-H(39E)	0.9600	C(53)-H(53A)	0.9600
C(39')-H(39F)	0.9600	C(53)-H(53B)	0.9600

Table 25 (con't).

Atoms	Distance	Atoms	Distance
C(53)-H(53C)	0.9600	O(1')-C(55')	1.319(15)
C(54)-H(54A)	0.9600	O(1')-C(58')	1.354(17)
C(54)-H(54B)	0.9600	C(55')-C(56')	1.528(15)
C(54)-H(54C)	0.9600	C(55')-H(55C)	0.9700
C(52')-C(53')	1.521(13)	C(55')-H(55D)	0.9700
C(52')-C(54')	1.530(13)	C(56')-C(57')	1.465(15)
C(52')-H(52')	0.9800	C(56')-H(56C)	0.9700
C(53')-H(53D)	0.9600	C(56')-H(56D)	0.9700
C(53')-H(53E)	0.9600	C(57')-C(58')	1.508(15)
C(53')-H(53F)	0.9600	C(57')-H(57C)	0.9700
C(54')-H(54D)	0.9600	C(57')-H(57D)	0.9700
C(54')-H(54E)	0.9600	C(58')-H(58C)	0.9700
C(54')-H(54F)	0.9600	C(58')-H(58D)	0.9700
O(1)-C(55)	1.306(13)	O(2)-C(59)	1.424(17)
O(1)-C(58)	1.379(12)	O(2)-C(62)	1.526(17)
C(55)-C(56)	1.526(12)	C(59)-C(60)	1.43(3)
C(55)-H(55A)	0.9700	C(59)-H(59A)	0.9700
C(55)-H(55B)	0.9700	C(59)-H(59B)	0.9700
C(56)-C(57)	1.456(17)	C(60)-C(61)	1.551(17)
C(56)-H(56A)	0.9700	C(60)-H(60A)	0.9700
C(56)-H(56B)	0.9700	C(60)-H(60B)	0.9700
C(57)-C(58)	1.509(12)	C(61)-C(62)	1.33(3)
C(57)-H(57A)	0.9700	C(61)-H(61A)	0.9700
C(57)-H(57B)	0.9700	C(61)-H(61B)	0.9700
C(58)-H(58A)	0.9700	C(62)-H(62A)	0.9700
C(58)-H(58B)	0.9700	C(62)-H(62B)	0.9700
C(1)-Si(1)-B(1')	112.2(6)		
C(1)-Si(1)-B(2)	107.7(2)		
B(1')-Si(1)-B(2)	136.1(6)		
C(1)-Si(1)-B(1)	107.2(2)		

Table 25 (con't).

Atoms	Distance	Atoms	Distance
Si(1)-C(1)	1.944(4)	C(6)-C(7)	1.360(8)
Si(1)-B(1')	1.966(17)	C(6)-H(6)	0.9300
Si(1)-B(2)	1.965(7)	C(7)-C(8)	1.371(8)
Si(1)-B(1)	1.994(8)	C(7)-H(7)	0.9300
Si(1)-H(1D)	1.49(4)	C(8)-C(9)	1.397(7)
Si(2)-B(1')	1.882(16)	C(8)-H(8)	0.9300
Si(2)-B(1)	1.922(7)	C(9)-C(10)	1.504(7)
Si(2)-C(28)	1.934(4)	C(10)-C(11)	1.516(8)
Si(2)-H(4D)	1.49(2)	C(10)-C(12)	1.537(8)
Si(2)-H(5D)	1.42(4)	C(10)-H(10)	0.9800
B(1)-H(2D)	1.145(19)	C(11)-H(11A)	0.9600
B(1)-H(3D)	1.119(19)	C(11)-H(11B)	0.9600
B(1')-H(3D)	1.155(19)	C(11)-H(11C)	0.9600
B(1')-H(2D')	1.15(2)	C(12)-H(12A)	0.9600
B(2)-B(3)	1.756(9)	C(12)-H(12B)	0.9600
B(2)-B(4)	1.811(11)	C(12)-H(12C)	0.9600
B(2)-H(6D)	1.278(19)	C(13)-C(15)	1.535(7)
B(2)-H(7D)	1.32(2)	C(13)-C(14)	1.549(7)
B(3)-B(4)	1.693(12)	C(13)-H(13)	0.9800
B(3)-H(8D)	1.383(19)	C(14)-H(14A)	0.9600
B(3)-H(9D)	1.12(5)	C(14)-H(14B)	0.9600
B(3)-H(10D)	1.09(7)	C(14)-H(14C)	0.9600
B(4)-H(10D)	1.59(2)	C(15)-H(15A)	0.9600
B(4)-H(11D)	1.31(2)	C(15)-H(15B)	0.9600
B(4)-H(12D)	1.26(2)	C(15)-H(15C)	0.9600
N(1)-C(1)	1.359(4)	C(16)-C(17)	1.384(6)
N(1)-C(2)	1.373(5)	C(16)-C(21)	1.392(6)
N(1)-C(16)	1.446(5)	C(17)-C(18)	1.407(7)
N(2)-C(1)	1.360(5)	C(17)-C(25)	1.504(7)
N(2)-C(3)	1.374(5)	C(18)-C(19)	1.343(8)
N(2)-C(4)	1.449(5)	C(18)-H(18)	0.9300
N(3)-C(28)	1.345(5)	C(19)-C(20)	1.362(8)
N(3)-C(29)	1.381(5)	C(19)-H(19)	0.9300
N(3)-C(43)	1.449(6)	C(20)-C(21)	1.406(6)
N(4)-C(28)	1.359(5)	C(20)-H(20)	0.9300
N(4)-C(30)	1.365(5)	C(21)-C(22)	1.518(7)
N(4)-C(31)	1.453(6)	C(22)-C(24)	1.530(7)
C(2)-C(3)	1.328(5)	C(22)-C(23)	1.527(7)
C(2)-H(2)	0.9300	C(22)-H(22)	0.9800
C(3)-H(3)	0.9300	C(23)-H(23A)	0.9600
C(4)-C(9)	1.388(6)	C(23)-H(23B)	0.9600
C(4)-C(5)	1.395(6)	C(23)-H(23C)	0.9600
C(5)-C(6)	1.373(7)	C(24)-H(24A)	0.9600
C(5)-C(13)	1.502(7)	C(24)-H(24B)	0.9600

Table 25 (con't).

Atoms	Distance	Atoms	Distance
C(24)-H(24C)	0.9600	C(40)-C(42)	1.539(14)
C(25)-C(26)	1.518(8)	C(40)-C(41)	1.545(19)
C(25)-C(27)	1.549(8)	C(40)-H(40)	0.9800
C(25)-H(25)	0.9800	C(41)-H(41A)	0.9600
C(26)-H(26A)	0.9600	C(41)-H(41B)	0.9600
C(26)-H(26B)	0.9600	C(41)-H(41C)	0.9600
C(26)-H(26C)	0.9600	C(42)-H(42A)	0.9600
C(27)-H(27A)	0.9600	C(42)-H(42B)	0.9600
C(27)-H(27B)	0.9600	C(42)-H(42C)	0.9600
C(27)-H(27C)	0.9600	C(40')-C(42')	1.516(16)
C(29)-C(30)	1.320(6)	C(40')-C(41')	1.525(17)
C(29)-H(29)	0.9300	C(40')-H(40')	0.9800
C(30)-H(30)	0.9300	C(41')-H(41D)	0.9600
C(31)-C(36)	1.379(8)	C(41')-H(41E)	0.9600
C(31)-C(32)	1.385(7)	C(41')-H(41F)	0.9600
C(32)-C(33)	1.398(9)	C(42')-H(42D)	0.9600
C(32)-C(40)	1.519(17)	C(42')-H(42E)	0.9600
C(32)-C(40')	1.533(15)	C(42')-H(42F)	0.9600
C(33)-C(34)	1.422(15)	C(43)-C(44)	1.380(7)
C(33)-H(33)	0.9300	C(43)-C(48)	1.381(7)
C(34)-C(35)	1.293(17)	C(44)-C(45)	1.375(8)
C(34)-H(34)	0.9300	C(44)-C(52')	1.528(15)
C(35)-C(36)	1.361(11)	C(44)-C(52)	1.570(12)
C(35)-H(35)	0.9300	C(45)-C(46)	1.345(9)
C(36)-C(37')	1.477(12)	C(45)-H(45)	0.9300
C(36)-C(37)	1.547(19)	C(46)-C(47)	1.353(9)
C(37)-C(38)	1.542(19)	C(46)-H(46)	0.9300
C(37)-C(39)	1.560(14)	C(47)-C(48)	1.391(8)
C(37)-H(37)	0.9800	C(47)-H(47)	0.9300
C(38)-H(38A)	0.9600	C(48)-C(49)	1.519(8)
C(38)-H(38B)	0.9600	C(49)-C(51)	1.503(9)
C(38)-H(38C)	0.9600	C(49)-C(50)	1.558(9)
C(39)-H(39A)	0.9600	C(49)-H(49)	0.9800
C(39)-H(39B)	0.9600	C(50)-H(50A)	0.9600
C(39)-H(39C)	0.9600	C(50)-H(50B)	0.9600
C(37')-C(38')	1.544(12)	C(50)-H(50C)	0.9600
C(37')-C(39')	1.560(11)	C(51)-H(51A)	0.9600
C(37')-H(37')	0.9800	C(51)-H(51B)	0.9600
C(38')-H(38D)	0.9600	C(51)-H(51C)	0.9600
C(38')-H(38E)	0.9600	C(52)-C(53)	1.529(12)
C(38')-H(38F)	0.9600	C(52)-C(54)	1.564(13)
C(39')-H(39D)	0.9600	C(52)-H(52)	0.9800
C(39')-H(39E)	0.9600	C(53)-H(53A)	0.9600
C(39')-H(39F)	0.9600	C(53)-H(53B)	0.9600

Table 25 (con't).

Atoms	Distance	Atoms	Distance
C(53)-H(53C)	0.9600	O(1')-C(55')	1.319(15)
C(54)-H(54A)	0.9600	O(1')-C(58')	1.354(17)
C(54)-H(54B)	0.9600	C(55')-C(56')	1.528(15)
C(54)-H(54C)	0.9600	C(55')-H(55C)	0.9700
C(52')-C(53')	1.521(13)	C(55')-H(55D)	0.9700
C(52')-C(54')	1.530(13)	C(56')-C(57')	1.465(15)
C(52')-H(52')	0.9800	C(56')-H(56C)	0.9700
C(53')-H(53D)	0.9600	C(56')-H(56D)	0.9700
C(53')-H(53E)	0.9600	C(57')-C(58')	1.508(15)
C(53')-H(53F)	0.9600	C(57')-H(57C)	0.9700
C(54')-H(54D)	0.9600	C(57')-H(57D)	0.9700
C(54')-H(54E)	0.9600	C(58')-H(58C)	0.9700
C(54')-H(54F)	0.9600	C(58')-H(58D)	0.9700
O(1)-C(55)	1.306(13)	O(2)-C(59)	1.424(17)
O(1)-C(58)	1.379(12)	O(2)-C(62)	1.526(17)
C(55)-C(56)	1.526(12)	C(59)-C(60)	1.43(3)
C(55)-H(55A)	0.9700	C(59)-H(59A)	0.9700
C(55)-H(55B)	0.9700	C(59)-H(59B)	0.9700
C(56)-C(57)	1.456(17)	C(60)-C(61)	1.551(17)
C(56)-H(56A)	0.9700	C(60)-H(60A)	0.9700
C(56)-H(56B)	0.9700	C(60)-H(60B)	0.9700
C(57)-C(58)	1.509(12)	C(61)-C(62)	1.33(3)
C(57)-H(57A)	0.9700	C(61)-H(61A)	0.9700
C(57)-H(57B)	0.9700	C(61)-H(61B)	0.9700
C(58)-H(58A)	0.9700	C(62)-H(62A)	0.9700
C(58)-H(58B)	0.9700	C(62)-H(62B)	0.9700
C(1)-Si(1)-B(1')	112.2(6)		
C(1)-Si(1)-B(2)	107.7(2)		
B(1')-Si(1)-B(2)	136.1(6)		
C(1)-Si(1)-B(1)	107.2(2)		

Table 26. Bond Angles [°] for **8**.

Atoms	Angle	Atoms	Angle
B(2)-Si(1)-B(1)	122.2(3)	B(4)-B(3)-H(9D)	121(3)
C(1)-Si(1)-H(1D)	95.3(14)	B(2)-B(3)-H(9D)	111(3)
B(1')-Si(1)-H(1D)	83.0(15)	H(8D)-B(3)-H(9D)	79(3)
B(2)-Si(1)-H(1D)	111.0(14)	B(4)-B(3)-H(10D)	65.3(14)
B(1)-Si(1)-H(1D)	109.9(14)	B(2)-B(3)-H(10D)	127.7(17)
B(1')-Si(2)-C(28)	122.1(6)	H(8D)-B(3)-H(10D)	121(3)
B(1)-Si(2)-C(28)	117.7(3)	H(9D)-B(3)-H(10D)	103(4)
B(1')-Si(2)-H(4D)	87(2)	B(3)-B(4)-B(2)	60.0(5)
B(1)-Si(2)-H(4D)	115(2)	B(3)-B(4)-H(10D)	39(3)
C(28)-Si(2)-H(4D)	96(2)	B(2)-B(4)-H(10D)	98(3)
B(1')-Si(2)-H(5D)	137.6(18)	B(3)-B(4)-H(11D)	121(3)
B(1)-Si(2)-H(5D)	123.6(17)	B(2)-B(4)-H(11D)	116(3)
C(28)-Si(2)-H(5D)	98.6(17)	H(10D)-B(4)-H(11D)	111(4)
H(4D)-Si(2)-H(5D)	101(3)	B(3)-B(4)-H(12D)	126(3)
Si(2)-B(1)-Si(1)	109.1(4)	B(2)-B(4)-H(12D)	113(3)
Si(2)-B(1)-H(2D)	110(2)	H(10D)-B(4)-H(12D)	107(4)
Si(1)-B(1)-H(2D)	108(2)	H(11D)-B(4)-H(12D)	110(4)
Si(2)-B(1)-H(3D)	114(2)	C(1)-N(1)-C(2)	110.6(3)
Si(1)-B(1)-H(3D)	110(2)	C(1)-N(1)-C(16)	128.1(3)
H(2D)-B(1)-H(3D)	106(3)	C(2)-N(1)-C(16)	121.2(3)
Si(2)-B(1)-Si(1)	112.0(10)	C(1)-N(2)-C(3)	110.9(3)
Si(2)-B(1)-H(3D)	114(2)	C(1)-N(2)-C(4)	128.0(3)
Si(1)-B(1)-H(3D)	110(2)	C(3)-N(2)-C(4)	120.8(3)
Si(2)-B(1')-H(2D')	86(8)	C(28)-N(3)-C(29)	110.5(4)
Si(1)-B(1')-H(2D')	106(8)	C(28)-N(3)-C(43)	126.7(4)
H(3D)-B(1')-H(2D')	127(8)	C(29)-N(3)-C(43)	122.2(4)
B(3)-B(2)-B(4)	56.6(5)	C(28)-N(4)-C(30)	111.0(4)
B(3)-B(2)-Si(1)	102.0(4)	C(28)-N(4)-C(31)	126.5(3)
B(4)-B(2)-Si(1)	124.6(4)	C(30)-N(4)-C(31)	122.3(4)
B(3)-B(2)-H(6D)	107(2)	N(1)-C(1)-N(2)	104.0(3)
B(4)-B(2)-H(6D)	122(2)	N(1)-C(1)-Si(1)	126.9(3)
Si(1)-B(2)-H(6D)	113(2)	N(2)-C(1)-Si(1)	129.1(3)
B(3)-B(2)-H(7D)	123(4)	C(3)-C(2)-N(1)	107.6(4)
B(4)-B(2)-H(7D)	72(4)	C(3)-C(2)-H(2)	126.2
Si(1)-B(2)-H(7D)	88(4)	N(1)-C(2)-H(2)	126.2
H(6D)-B(2)-H(7D)	120(4)	C(2)-C(3)-N(2)	106.9(4)
B(4)-B(3)-B(2)	63.3(5)	C(2)-C(3)-H(3)	126.5
B(4)-B(3)-H(8D)	158.0(19)	N(2)-C(3)-H(3)	126.5
B(2)-B(3)-H(8D)	104.0(19)		

Table 26 (con't).

Atoms	Angle	Atoms	Angle
C(9)-C(4)-C(5)	123.0(4)	C(5)-C(13)-C(14)	113.2(5)
C(9)-C(4)-N(2)	118.6(4)	C(15)-C(13)-C(14)	110.1(5)
C(5)-C(4)-N(2)	118.1(4)	C(5)-C(13)-H(13)	107.7
C(6)-C(5)-C(4)	117.1(5)	C(15)-C(13)-H(13)	107.7
C(6)-C(5)-C(13)	119.7(5)	C(14)-C(13)-H(13)	107.7
C(4)-C(5)-C(13)	123.1(4)	C(13)-C(14)-H(14A)	109.5
C(7)-C(6)-C(5)	121.9(6)	C(13)-C(14)-H(14B)	109.5
C(7)-C(6)-H(6)	119.0	H(14A)-C(14)-H(14B)	109.5
C(5)-C(6)-H(6)	119.0	C(13)-C(14)-H(14C)	109.5
C(6)-C(7)-C(8)	120.2(6)	H(14A)-C(14)-H(14C)	109.5
C(6)-C(7)-H(7)	119.9	H(14B)-C(14)-H(14C)	109.5
C(8)-C(7)-H(7)	119.9	C(13)-C(15)-H(15A)	109.5
C(7)-C(8)-C(9)	121.2(6)	C(13)-C(15)-H(15B)	109.5
C(7)-C(8)-H(8)	119.4	H(15A)-C(15)-H(15B)	109.5
C(9)-C(8)-H(8)	119.4	C(13)-C(15)-H(15C)	109.5
C(4)-C(9)-C(8)	116.6(5)	H(15A)-C(15)-H(15C)	109.5
C(4)-C(9)-C(10)	122.8(4)	H(15B)-C(15)-H(15C)	109.5
C(8)-C(9)-C(10)	120.5(5)	C(17)-C(16)-C(21)	123.1(5)
C(9)-C(10)-C(11)	110.8(5)	C(17)-C(16)-N(1)	118.6(5)
C(9)-C(10)-C(12)	114.3(5)	C(21)-C(16)-N(1)	118.0(4)
C(11)-C(10)-C(12)	107.8(5)	C(16)-C(17)-C(18)	117.7(5)
C(9)-C(10)-H(10)	107.9	C(16)-C(17)-C(25)	122.4(5)
C(11)-C(10)-H(10)	107.9	C(18)-C(17)-C(25)	119.9(6)
C(12)-C(10)-H(10)	107.9	C(19)-C(18)-C(17)	120.1(6)
C(10)-C(11)-H(11A)	109.5	C(19)-C(18)-H(18)	119.9
C(10)-C(11)-H(11B)	109.5	C(17)-C(18)-H(18)	119.9
H(11A)-C(11)-H(11B)	109.5	C(18)-C(19)-C(20)	121.7(6)
C(10)-C(11)-H(11C)	109.5	C(18)-C(19)-H(19)	119.2
H(11A)-C(11)-H(11C)	109.5	C(20)-C(19)-H(19)	119.2
H(11B)-C(11)-H(11C)	109.5	C(19)-C(20)-C(21)	121.4(6)
C(10)-C(12)-H(12A)	109.5	C(19)-C(20)-H(20)	119.3
C(10)-C(12)-H(12B)	109.5	C(21)-C(20)-H(20)	119.3
H(12A)-C(12)-H(12B)	109.5	C(16)-C(21)-C(20)	115.9(5)
C(10)-C(12)-H(12C)	109.5	C(16)-C(21)-C(22)	123.9(4)
H(12A)-C(12)-H(12C)	109.5	C(20)-C(21)-C(22)	120.1(5)
H(12B)-C(12)-H(12C)	109.5	C(24)-C(22)-C(23)	111.5(5)
C(5)-C(13)-C(15)	110.3(5)	C(24)-C(22)-C(21)	110.4(4)

Table 26 (con't).

Atoms	Angle	Atoms	Angle
C(23)-C(22)-C(21)	113.4(4)	N(4)-C(30)-H(30)	126.5
C(24)-C(22)-H(22)	107.1	C(36)-C(31)-C(32)	124.8(6)
C(23)-C(22)-H(22)	107.1	C(36)-C(31)-N(4)	116.5(6)
C(21)-C(22)-H(22)	107.1	C(32)-C(31)-N(4)	118.6(5)
C(22)-C(23)-H(23A)	109.5	C(31)-C(32)-C(33)	115.9(7)
C(22)-C(23)-H(23B)	109.5	C(31)-C(32)-C(40)	122.5(12)
H(23A)-C(23)-H(23B)	109.5	C(33)-C(32)-C(40)	119.5(12)
C(22)-C(23)-H(23C)	109.5	C(31)-C(32)-C(40')	119.9(9)
H(23A)-C(23)-H(23C)	109.5	C(33)-C(32)-C(40')	122.9(11)
H(23B)-C(23)-H(23C)	109.5	C(40)-C(32)-C(40')	24.8(10)
C(22)-C(24)-H(24A)	109.5	C(32)-C(33)-C(34)	118.0(9)
C(22)-C(24)-H(24B)	109.5	C(32)-C(33)-H(33)	121.0
H(24A)-C(24)-H(24B)	109.5	C(34)-C(33)-H(33)	121.0
C(22)-C(24)-H(24C)	109.5	C(35)-C(34)-C(33)	122.0(12)
H(24A)-C(24)-H(24C)	109.5	C(35)-C(34)-H(34)	119.0
H(24B)-C(24)-H(24C)	109.5	C(33)-C(34)-H(34)	119.0
C(17)-C(25)-C(26)	112.5(5)	C(34)-C(35)-C(36)	122.3(14)
C(17)-C(25)-C(27)	111.1(6)	C(34)-C(35)-H(35)	118.8
C(26)-C(25)-C(27)	109.1(5)	C(36)-C(35)-H(35)	118.8
C(17)-C(25)-H(25)	108.0	C(31)-C(36)-C(35)	116.2(9)
C(26)-C(25)-H(25)	108.0	C(31)-C(36)-C(37')	127.2(10)
C(27)-C(25)-H(25)	108.0	C(35)-C(36)-C(37')	116.5(12)
C(25)-C(26)-H(26A)	109.5	C(31)-C(36)-C(37)	115.6(18)
C(25)-C(26)-H(26B)	109.5	C(35)-C(36)-C(37)	128(2)
H(26A)-C(26)-H(26B)	109.5	C(38)-C(37)-C(36)	98(3)
C(25)-C(26)-H(26C)	109.5	C(38)-C(37)-C(39)	108.7(19)
H(26A)-C(26)-H(26C)	109.5	C(36)-C(37)-C(39)	131(4)
H(26B)-C(26)-H(26C)	109.5	C(38)-C(37)-H(37)	105.6
C(25)-C(27)-H(27A)	109.5	C(36)-C(37)-H(37)	105.6
C(25)-C(27)-H(27B)	109.5	C(39)-C(37)-H(37)	105.6
H(27A)-C(27)-H(27B)	109.5	C(37)-C(38)-H(38A)	109.5
C(25)-C(27)-H(27C)	109.5	C(37)-C(38)-H(38B)	109.5
H(27A)-C(27)-H(27C)	109.5	H(38A)-C(38)-H(38B)	109.5
H(27B)-C(27)-H(27C)	109.5	C(37)-C(38)-H(38C)	109.5
N(3)-C(28)-N(4)	104.0(3)	H(38A)-C(38)-H(38C)	109.5
N(3)-C(28)-Si(2)	128.8(3)	H(38B)-C(38)-H(38C)	109.5
N(4)-C(28)-Si(2)	127.2(3)	C(37)-C(39)-H(39A)	109.5
C(30)-C(29)-N(3)	107.3(4)	C(37)-C(39)-H(39B)	109.5
C(30)-C(29)-H(29)	126.3	H(39A)-C(39)-H(39B)	109.5
N(3)-C(29)-H(29)	126.3	C(37)-C(39)-H(39C)	109.5
C(29)-C(30)-N(4)	107.1(4)	H(39A)-C(39)-H(39C)	109.5
C(29)-C(30)-H(30)	126.5	H(39B)-C(39)-H(39C)	109.5

Table 26 (con't).

Atoms	Angle	Atoms	Angle
C(36)-C(37')-C(38')	118.0(15)	H(41D)-C(41')-H(41E)	109.5
C(36)-C(37')-C(39')	105.9(13)	C(40')-C(41')-H(41F)	109.5
C(38')-C(37')-C(39')	108.9(12)	H(41D)-C(41')-H(41F)	109.5
C(36)-C(37')-H(37')	107.9	H(41E)-C(41')-H(41F)	109.5
C(38')-C(37')-H(37')	107.9	C(40')-C(42')-H(42D)	109.5
C(39')-C(37')-H(37')	107.9	C(40')-C(42')-H(42E)	109.5
C(37')-C(38')-H(38D)	109.5	H(42D)-C(42')-H(42E)	109.5
C(37')-C(38')-H(38E)	109.5	C(40')-C(42')-H(42F)	109.5
H(38D)-C(38')-H(38E)	109.5	H(42D)-C(42')-H(42F)	109.5
C(37')-C(38')-H(38F)	109.5	H(42E)-C(42')-H(42F)	109.5
H(38D)-C(38')-H(38F)	109.5	C(44)-C(43)-C(48)	123.3(5)
H(38E)-C(38')-H(38F)	109.5	C(44)-C(43)-N(3)	119.0(5)
C(37')-C(39')-H(39D)	109.5	C(48)-C(43)-N(3)	117.4(5)
C(37')-C(39')-H(39E)	109.5	C(45)-C(44)-C(43)	116.8(6)
H(39D)-C(39')-H(39E)	109.5	C(45)-C(44)-C(52')	123.7(9)
C(37')-C(39')-H(39F)	109.5	C(43)-C(44)-C(52')	114.2(10)
H(39D)-C(39')-H(39F)	109.5	C(45)-C(44)-C(52)	116.7(9)
H(39E)-C(39')-H(39F)	109.5	C(43)-C(44)-C(52)	125.5(7)
C(32)-C(40)-C(42)	110.9(17)	C(46)-C(45)-C(44)	121.6(7)
C(32)-C(40)-C(41)	98(2)	C(46)-C(45)-H(45)	119.2
C(42)-C(40)-C(41)	108.4(16)	C(44)-C(45)-H(45)	119.2
C(32)-C(40)-H(40)	112.9	C(45)-C(46)-C(47)	120.8(7)
C(42)-C(40)-H(40)	112.9	C(45)-C(46)-H(46)	119.6
C(41)-C(40)-H(40)	112.9	C(47)-C(46)-H(46)	119.6
C(40)-C(41)-H(41A)	109.5	C(46)-C(47)-C(48)	121.2(7)
C(40)-C(41)-H(41B)	109.5	C(46)-C(47)-H(47)	119.4
H(41A)-C(41)-H(41B)	109.5	C(48)-C(47)-H(47)	119.4
C(40)-C(41)-H(41C)	109.5	C(43)-C(48)-C(47)	116.2(6)
H(41A)-C(41)-H(41C)	109.5	C(43)-C(48)-C(49)	122.2(5)
H(41B)-C(41)-H(41C)	109.5	C(47)-C(48)-C(49)	121.6(6)
C(40)-C(42)-H(42A)	109.5	C(51)-C(49)-C(48)	112.3(6)
C(40)-C(42)-H(42B)	109.5	C(51)-C(49)-C(50)	109.0(7)
H(42A)-C(42)-H(42B)	109.5	C(48)-C(49)-C(50)	110.5(7)
C(40)-C(42)-H(42C)	109.5	C(51)-C(49)-H(49)	108.3
H(42A)-C(42)-H(42C)	109.5	C(48)-C(49)-H(49)	108.3
H(42B)-C(42)-H(42C)	109.5	C(50)-C(49)-H(49)	108.3
C(42')-C(40')-C(32)	110.8(17)	C(49)-C(50)-H(50A)	109.5
C(42')-C(40')-C(41')	112.2(14)	C(49)-C(50)-H(50B)	109.5
C(32)-C(40')-C(41')	120(2)	H(50A)-C(50)-H(50B)	109.5
C(42')-C(40')-H(40')	104.1	C(49)-C(50)-H(50C)	109.5
C(32)-C(40')-H(40')	104.1	H(50A)-C(50)-H(50C)	109.5
C(41')-C(40')-H(40')	104.1	H(50B)-C(50)-H(50C)	109.5
C(40')-C(41')-H(41D)	109.5	C(49)-C(51)-H(51A)	109.5
C(40')-C(41')-H(41E)	109.5	C(49)-C(51)-H(51B)	109.5

Table 26 (con't).

Atoms	Angle	Atoms	Angle
H(51A)-C(51)-H(51B)	109.5	O(1)-C(55)-H(55B)	110.5
C(49)-C(51)-H(51C)	109.5	C(56)-C(55)-H(55B)	110.5
H(51A)-C(51)-H(51C)	109.5	H(55A)-C(55)-H(55B)	108.7
H(51B)-C(51)-H(51C)	109.5	C(57)-C(56)-C(55)	103.8(14)
C(53)-C(52)-C(54)	109.4(10)	C(57)-C(56)-H(56A)	111.0
C(53)-C(52)-C(44)	109.2(12)	C(55)-C(56)-H(56A)	111.0
C(54)-C(52)-C(44)	121.1(13)	C(57)-C(56)-H(56B)	111.0
C(53)-C(52)-H(52)	105.3	C(55)-C(56)-H(56B)	111.0
C(54)-C(52)-H(52)	105.3	H(56A)-C(56)-H(56B)	109.0
C(44)-C(52)-H(52)	105.3	C(56)-C(57)-C(58)	103.1(13)
C(52)-C(53)-H(53A)	109.5	C(56)-C(57)-H(57A)	111.1
C(52)-C(53)-H(53B)	109.5	C(58)-C(57)-H(57A)	111.1
H(53A)-C(53)-H(53B)	109.5	C(56)-C(57)-H(57B)	111.1
C(52)-C(53)-H(53C)	109.5	C(58)-C(57)-H(57B)	111.1
H(53A)-C(53)-H(53C)	109.5	H(57A)-C(57)-H(57B)	109.1
H(53B)-C(53)-H(53C)	109.5	O(1)-C(58)-C(57)	107.6(13)
C(52)-C(54)-H(54A)	109.5	O(1)-C(58)-H(58A)	110.2
C(52)-C(54)-H(54B)	109.5	C(57)-C(58)-H(58A)	110.2
H(54A)-C(54)-H(54B)	109.5	O(1)-C(58)-H(58B)	110.2
C(52)-C(54)-H(54C)	109.5	C(57)-C(58)-H(58B)	110.2
H(54A)-C(54)-H(54C)	109.5	H(58A)-C(58)-H(58B)	108.5
H(54B)-C(54)-H(54C)	109.5	C(55')-O(1')-C(58')	107.8(17)
C(53')-C(52')-C(54')	109.2(13)	O(1')-C(55')-C(56')	108.7(18)
C(53')-C(52')-C(44)	118.6(15)	O(1')-C(55')-H(55C)	110.0
C(54')-C(52')-C(44)	94.0(16)	C(56')-C(55')-H(55C)	110.0
C(53')-C(52')-H(52')	111.2	O(1')-C(55')-H(55D)	110.0
C(54')-C(52')-H(52')	111.2	C(56')-C(55')-H(55D)	110.0
C(44)-C(52')-H(52')	111.2	H(55C)-C(55')-H(55D)	108.3
C(52')-C(53')-H(53D)	109.5	C(57')-C(56')-C(55')	103.1(15)
C(52')-C(53')-H(53E)	109.5	C(57')-C(56')-H(56C)	111.2
H(53D)-C(53')-H(53E)	109.5	C(55')-C(56')-H(56C)	111.2
C(52')-C(53')-H(53F)	109.5	C(57')-C(56')-H(56D)	111.2
H(53D)-C(53')-H(53F)	109.5	C(55')-C(56')-H(56D)	111.2
H(53E)-C(53')-H(53F)	109.5	H(56C)-C(56')-H(56D)	109.1
C(52')-C(54')-H(54D)	109.5	C(56')-C(57')-C(58')	101.1(16)
C(52')-C(54')-H(54E)	109.5	C(56')-C(57')-H(57C)	111.6
H(54D)-C(54')-H(54E)	109.5	C(58')-C(57')-H(57C)	111.6
C(52')-C(54')-H(54F)	109.5	C(56')-C(57')-H(57D)	111.6
H(54D)-C(54')-H(54F)	109.5	C(58')-C(57')-H(57D)	111.6
H(54E)-C(54')-H(54F)	109.5	H(57C)-C(57')-H(57D)	109.4
C(55)-O(1)-C(58)	111.7(13)	O(1')-C(58')-C(57')	106(2)
O(1)-C(55)-C(56)	105.9(14)	O(1')-C(58')-H(58C)	110.5
O(1)-C(55)-H(55A)	110.5	C(57')-C(58')-H(58C)	110.5
C(56)-C(55)-H(55A)	110.5	O(1')-C(58')-H(58D)	110.5

Table 26 (con't).

Atoms	Angle	Atoms	Angle
C(57')-C(58')-H(58D)	110.5	H(60A)-C(60)-H(60B)	111.7
H(58C)-C(58')-H(58D)	108.7	C(62)-C(61)-C(60)	112(3)
C(59)-O(2)-C(62)	98.4(15)	C(62)-C(61)-H(61A)	109.1
C(60)-C(59)-O(2)	120.6(18)	C(60)-C(61)-H(61A)	109.1
C(60)-C(59)-H(59A)	107.2	C(59)-C(61)-H(61A)	90.3
O(2)-C(59)-H(59A)	107.2	C(62)-C(61)-H(61B)	109.1
C(61)-C(59)-H(59A)	108.4	C(60)-C(61)-H(61B)	109.1
C(60)-C(59)-H(59B)	107.2	C(59)-C(61)-H(61B)	153.6
O(2)-C(59)-H(59B)	107.2	H(61A)-C(61)-H(61B)	107.8
C(61)-C(59)-H(59B)	142.8	C(61)-C(62)-O(2)	95(2)
H(59A)-C(59)-H(59B)	106.8	C(61)-C(62)-H(62A)	112.8
C(59)-C(60)-C(61)	84.3(19)	O(2)-C(62)-H(62A)	112.8
C(59)-C(60)-H(60A)	114.6	C(61)-C(62)-H(62B)	112.8
C(61)-C(60)-H(60A)	114.6	O(2)-C(62)-H(62B)	112.8
C(59)-C(60)-H(60B)	114.6	H(62A)-C(62)-H(62B)	110.3
C(61)-C(60)-H(60B)	114.6		

Structural Data for compound containing three-membered cyclic silylene **9**.

Table 27. Crystal data and structure refinement for **9**.

Empirical formula	C ₅₈ H ₈₈ B ₂ N ₄ O ₂ Si
Formula weight	923.03
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pna2(1)
Unit cell dimensions	a = 20.195(6) Å b = 12.590(4) Å c = 22.879(6) Å α= 90° β = 90° γ = 90°
Volume	5817(3) Å ³
Z, Calculated density	4, 1.054 Mg/m ³
Absorption coefficient	0.082 mm ⁻¹
F(000)	2016
Crystal size	0.15 x 0.12 x 0.09 mm
Theta range for data collection	2.02 to 25.00°
Limiting indices	-24<=h<=24, -14<=k<=14, -27<=l<=27
Reflections collected / unique	60732 / 10230 [R(int) = 0.0699]
Completeness to theta =	25.00 99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9927 and 0.9878
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10230 / 77 / 665
Goodness-of-fit on F ²	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.1162
R indices (all data)	R1 = 0.0892, wR2 = 0.1357
Absolute structure parameter	-0.08(13)
Largest diff. peak and hole	0.165 and -0.182 e.Å ⁻³

Table 28. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **9**.

Atom	X	Y	Z	U(eq)
Si(1)	6011(1)	4849(1)	4265(1)	45(1)
B(1)	4880(2)	4338(3)	6145(2)	67(1)
B(2)	6898(2)	4313(4)	4511(2)	73(1)
N(1)	4951(1)	4003(2)	5020(1)	44(1)
N(2)	5299(1)	5556(2)	5296(1)	44(1)
N(3)	6120(1)	4697(2)	2996(1)	50(1)
N(4)	5732(1)	6230(2)	3215(1)	48(1)
C(1)	5050(1)	4630(2)	5484(1)	44(1)
C(2)	5121(2)	4512(2)	4464(1)	45(1)
C(3)	5343(2)	5621(2)	4655(1)	46(1)
C(4)	5402(2)	6508(2)	5640(1)	56(1)
C(5)	4877(2)	7221(3)	5684(2)	74(1)
C(6)	5020(3)	8207(3)	5950(2)	105(2)
C(7)	5660(4)	8414(4)	6160(2)	124(2)
C(8)	6136(3)	7676(4)	6130(2)	106(2)
C(9)	6027(2)	6714(3)	5876(2)	72(1)
C(10)	6566(2)	5891(4)	5883(2)	93(1)
C(11)	7245(2)	6292(5)	5722(3)	145(2)
C(12)	6610(3)	5408(6)	6501(3)	173(3)
C(13)	4182(2)	6958(3)	5504(2)	86(1)
C(14)	3737(3)	6793(5)	6036(3)	129(2)
C(15)	3873(3)	7808(5)	5116(3)	145(2)
C(16)	4643(2)	2971(2)	5028(1)	52(1)
C(17)	3965(2)	2905(2)	4915(2)	60(1)
C(18)	3682(2)	1893(3)	4894(2)	78(1)
C(19)	4059(2)	1010(3)	4974(2)	80(1)
C(20)	4714(2)	1088(2)	5092(2)	72(1)
C(21)	5033(2)	2075(2)	5121(1)	56(1)
C(22)	5768(2)	2128(3)	5244(2)	72(1)
C(23)	5940(3)	1692(5)	5852(2)	131(2)
C(24)	6162(2)	1588(4)	4771(2)	114(2)
C(25)	3529(2)	3865(3)	4823(2)	81(1)
C(26)	3143(2)	3813(4)	4246(2)	108(1)
C(27)	3054(2)	4013(4)	5336(3)	124(2)
C(28)	5930(1)	5291(2)	3456(1)	44(1)
C(29)	6032(2)	5244(3)	2484(1)	67(1)
C(30)	5792(2)	6193(3)	2618(1)	64(1)
C(31)	5450(2)	7154(2)	3492(1)	57(1)
C(32)	4769(2)	7314(3)	3413(2)	70(1)
C(33)	4509(3)	8250(4)	3629(2)	105(2)
C(34)	4898(4)	8968(4)	3906(2)	132(3)
C(35)	5555(4)	8794(4)	3984(2)	114(2)

Table 28 (con't).

Atom	X	Y	Z	U(eq)
C(36)	5857(2)	7867(3)	3773(2)	81(1)
C(37)	6613(8)	7869(19)	3850(9)	101(6)
C(38)	6770(20)	8330(30)	4456(10)	157(11)
C(39)	6839(9)	8740(20)	3417(9)	139(7)
C(37')	6578(7)	7571(15)	3813(7)	109(5)
C(38')	6968(14)	7930(20)	4346(7)	149(8)
C(39')	7015(7)	7840(20)	3286(5)	154(8)
C(40)	4324(2)	6534(4)	3110(2)	93(1)
C(41)	3782(3)	6134(5)	3522(3)	158(3)
C(42)	4028(3)	7009(6)	2554(3)	139(2)
C(43)	6385(2)	3629(2)	3004(1)	59(1)
C(44)	5946(2)	2790(3)	3051(2)	68(1)
C(45)	6220(3)	1772(3)	3032(2)	104(2)
C(46)	6892(3)	1638(4)	2962(3)	122(2)
C(47)	7307(2)	2487(4)	2901(2)	105(2)
C(48)	7069(2)	3514(3)	2928(2)	69(1)
C(49)	7538(2)	4426(3)	2850(2)	81(1)
C(50)	8151(2)	4347(5)	3247(3)	128(2)
C(51)	7747(3)	4560(5)	2213(3)	141(2)
C(52)	5201(2)	2945(3)	3084(2)	72(1)
C(53)	4853(2)	2109(4)	3458(2)	106(2)
C(54)	4903(2)	2946(5)	2475(2)	119(2)
C(55)	5265(10)	9477(8)	2281(5)	431(15)
O(1)	5654(3)	8656(6)	2081(3)	210(3)
C(56)	6029(8)	9200(12)	1644(5)	302(8)
C(57)	6467(7)	8448(11)	1463(4)	254(6)
O(2)	6872(5)	8157(9)	1888(4)	289(4)
C(58)	7433(8)	7476(12)	1731(8)	354(9)

Table 29. Bond lengths [Å] for **9**.

Atoms	Distance	Atoms	Distance
Si(1)-C(3)	1.888(3)	C(12)-H(12B)	0.9600
Si(1)-C(2)	1.903(3)	C(12)-H(12C)	0.9600
Si(1)-C(28)	1.938(3)	C(13)-C(15)	1.524(6)
Si(1)-B(2)	1.996(4)	C(13)-C(14)	1.527(7)
B(1)-C(1)	1.593(5)	C(13)-H(13)	0.9800
B(1)-H(1A)	1.126(19)	C(14)-H(14A)	0.9600
B(1)-H(1B)	1.143(19)	C(14)-H(14B)	0.9600
B(1)-H(1C)	1.16(2)	C(14)-H(14C)	0.9600
B(2)-H(2A)	1.117(18)	C(15)-H(15A)	0.9600
B(2)-H(2B)	1.134(19)	C(15)-H(15B)	0.9600
B(2)-H(2C)	1.175(19)	C(15)-H(15C)	0.9600
N(1)-C(1)	1.339(3)	C(16)-C(21)	1.393(4)
N(1)-C(16)	1.441(3)	C(16)-C(17)	1.396(4)
N(1)-C(2)	1.466(4)	C(17)-C(18)	1.397(5)
N(2)-C(1)	1.340(4)	C(17)-C(25)	1.510(5)
N(2)-C(4)	1.448(4)	C(18)-C(19)	1.360(5)
N(2)-C(3)	1.473(4)	C(18)-H(18)	0.9300
N(3)-C(28)	1.348(4)	C(19)-C(20)	1.353(5)
N(3)-C(29)	1.371(4)	C(19)-H(19)	0.9300
N(3)-C(43)	1.447(4)	C(20)-C(21)	1.401(4)
N(4)-C(28)	1.365(4)	C(20)-H(20)	0.9300
N(4)-C(30)	1.372(4)	C(21)-C(22)	1.511(5)
N(4)-C(31)	1.443(4)	C(22)-C(24)	1.506(6)
C(2)-C(3)	1.530(4)	C(22)-C(23)	1.535(6)
C(2)-H(2)	0.97(3)	C(22)-H(22)	0.9800
C(3)-H(3)	0.93(3)	C(23)-H(23A)	0.9600
C(4)-C(5)	1.392(5)	C(23)-H(23B)	0.9600
C(4)-C(9)	1.397(5)	C(23)-H(23C)	0.9600
C(5)-C(6)	1.413(6)	C(24)-H(24A)	0.9600
C(5)-C(13)	1.500(6)	C(24)-H(24B)	0.9600
C(6)-C(7)	1.404(8)	C(24)-H(24C)	0.9600
C(6)-H(6)	0.9300	C(25)-C(27)	1.528(6)
C(7)-C(8)	1.339(8)	C(25)-C(26)	1.534(6)
C(7)-H(7)	0.9300	C(25)-H(25)	0.9800
C(8)-C(9)	1.361(5)	C(26)-H(26A)	0.9600
C(8)-H(8)	0.9300	C(26)-H(26B)	0.9600
C(9)-C(10)	1.503(6)	C(26)-H(26C)	0.9600
C(10)-C(11)	1.506(6)	C(27)-H(27A)	0.9600
C(10)-C(12)	1.541(8)	C(27)-H(27B)	0.9600
C(10)-H(10)	0.9800	C(27)-H(27C)	0.9600
C(11)-H(11A)	0.9600	C(29)-C(30)	1.326(5)
C(11)-H(11B)	0.9600	C(29)-H(29)	0.9300
C(11)-H(11C)	0.9600	C(30)-H(30)	0.9300
C(12)-H(12A)	0.9600	C(31)-C(36)	1.376(5)

Table 29 (con't).

Atoms	Distance	Atoms	Distance
C(31)-C(32)	1.400(5)	C(44)-C(52)	1.519(5)
C(32)-C(33)	1.383(5)	C(45)-C(46)	1.377(6)
C(32)-C(40)	1.502(6)	C(45)-H(45)	0.9300
C(33)-C(34)	1.355(8)	C(46)-C(47)	1.366(6)
C(33)-H(33)	0.9300	C(46)-H(46)	0.9300
C(34)-C(35)	1.356(8)	C(47)-C(48)	1.382(5)
C(34)-H(34)	0.9300	C(47)-H(47)	0.9300
C(35)-C(36)	1.404(7)	C(48)-C(49)	1.499(5)
C(35)-H(35)	0.9300	C(49)-C(51)	1.527(6)
C(36)-C(37')	1.505(14)	C(49)-C(50)	1.538(6)
C(36)-C(37)	1.537(16)	C(49)-H(49)	0.9800
C(37)-C(38)	1.533(13)	C(50)-H(50A)	0.9600
C(37)-C(39)	1.549(13)	C(50)-H(50B)	0.9600
C(37)-H(37)	0.9800	C(50)-H(50C)	0.9600
C(38)-H(38A)	0.9600	C(51)-H(51A)	0.9600
C(38)-H(38B)	0.9600	C(51)-H(51B)	0.9600
C(38)-H(38C)	0.9600	C(51)-H(51C)	0.9600
C(39)-H(39A)	0.9600	C(52)-C(54)	1.519(6)
C(39)-H(39B)	0.9600	C(52)-C(53)	1.528(5)
C(39)-H(39C)	0.9600	C(52)-H(52)	0.9800
C(37')-C(38')	1.521(14)	C(53)-H(53A)	0.9600
C(37')-C(39')	1.534(13)	C(53)-H(53B)	0.9600
C(37')-H(37')	0.9800	C(53)-H(53C)	0.9600
C(38')-H(38D)	0.9600	C(54)-H(54A)	0.9600
C(38')-H(38E)	0.9600	C(54)-H(54B)	0.9600
C(38')-H(38F)	0.9600	C(54)-H(54C)	0.9600
C(39')-H(39D)	0.9600	C(55)-O(1)	1.376(12)
C(39')-H(39E)	0.9600	C(55)-H(55A)	0.9600
C(39')-H(39F)	0.9600	C(55)-H(55B)	0.9600
C(40)-C(42)	1.526(7)	C(55)-H(55C)	0.9600
C(40)-C(41)	1.531(7)	O(1)-C(56)	1.430(12)
C(40)-H(40)	0.9800	C(56)-C(57)	1.360(11)
C(41)-H(41A)	0.9600	C(56)-H(56A)	0.9700
C(41)-H(41B)	0.9600	C(56)-H(56B)	0.9700
C(41)-H(41C)	0.9600	C(57)-O(2)	1.322(10)
C(42)-H(42A)	0.9600	C(57)-H(57A)	0.9700
C(42)-H(42B)	0.9600	C(57)-H(57B)	0.9700
C(42)-H(42C)	0.9600	O(2)-C(58)	1.465(13)
C(43)-C(44)	1.383(5)	C(58)-H(58A)	0.9600
C(43)-C(48)	1.400(5)	C(58)-H(58B)	0.9600
C(44)-C(45)	1.396(5)	C(58)-H(58C)	0.9600

Table 30. Bond angles [°] for **9**.

Atoms	Angle	Atoms	Angle
C(3)-Si(1)-C(2)	47.62(12)	Si(1)-C(3)-H(3)	121.7(17)
C(3)-Si(1)-C(28)	104.04(1)	C(5)-C(4)-C(9)	122.7(3)
C(2)-Si(1)-C(28)	102.27(1)	C(5)-C(4)-N(2)	117.5(3)
C(3)-Si(1)-B(2)	133.06(1)	C(9)-C(4)-N(2)	119.6(3)
C(2)-Si(1)-B(2)	134.88(1)	C(4)-C(5)-C(6)	116.2(4)
C(28)-Si(1)-B(2)	116.25(1)	C(4)-C(5)-C(13)	123.4(3)
C(1)-B(1)-H(1A)	107(2)	C(6)-C(5)-C(13)	120.2(4)
C(1)-B(1)-H(1B)	109(2)	C(7)-C(6)-C(5)	120.0(5)
H(1A)-B(1)-H(1B)	116(3)	C(7)-C(6)-H(6)	120.0
C(1)-B(1)-H(1C)	111(3)	C(5)-C(6)-H(6)	120.0
H(1A)-B(1)-H(1C)	115(3)	C(8)-C(7)-C(6)	120.9(4)
H(1B)-B(1)-H(1C)	98(3)	C(8)-C(7)-H(7)	119.5
Si(1)-B(2)-H(2A)	108.3(17)	C(6)-C(7)-H(7)	119.5
Si(1)-B(2)-H(2B)	109.1(18)	C(7)-C(8)-C(9)	121.6(5)
H(2A)-B(2)-H(2B)	108(3)	C(7)-C(8)-H(8)	119.2
Si(1)-B(2)-H(2C)	105(2)	C(9)-C(8)-H(8)	119.2
H(2A)-B(2)-H(2C)	114(3)	C(8)-C(9)-C(4)	118.4(4)
H(2B)-B(2)-H(2C)	112(3)	C(8)-C(9)-C(10)	119.4(4)
C(1)-N(1)-C(16)	125.9(2)	C(4)-C(9)-C(10)	122.1(3)
C(1)-N(1)-C(2)	113.3(2)	C(9)-C(10)-C(11)	115.2(4)
C(16)-N(1)-C(2)	120.4(2)	C(9)-C(10)-C(12)	109.0(4)
C(1)-N(2)-C(4)	126.8(2)	C(11)-C(10)-C(12)	107.7(4)
C(1)-N(2)-C(3)	113.0(2)	C(9)-C(10)-H(10)	108.3
C(4)-N(2)-C(3)	119.2(2)	C(11)-C(10)-H(10)	108.3
C(28)-N(3)-C(29)	110.6(2)	C(12)-C(10)-H(10)	108.3
C(28)-N(3)-C(43)	127.7(3)	C(10)-C(11)-H(11A)	109.5
C(29)-N(3)-C(43)	121.7(3)	C(10)-C(11)-H(11B)	109.5
C(28)-N(4)-C(30)	110.4(3)	H(11A)-C(11)-H(11B)	109.5
C(28)-N(4)-C(31)	129.5(2)	C(10)-C(11)-H(11C)	109.5
C(30)-N(4)-C(31)	120.0(3)	H(11A)-C(11)-H(11C)	109.5
N(1)-C(1)-N(2)	108.4(2)	H(11B)-C(11)-H(11C)	109.5
N(1)-C(1)-B(1)	125.7(3)	C(10)-C(12)-H(12A)	109.5
N(2)-C(1)-B(1)	125.9(3)	C(10)-C(12)-H(12B)	109.5
N(1)-C(2)-C(3)	102.7(2)	H(12A)-C(12)-H(12B)	109.5
N(1)-C(2)-Si(1)	121.8(2)	C(10)-C(12)-H(12C)	109.5
C(3)-C(2)-Si(1)	65.68(16)	H(12A)-C(12)-H(12C)	109.5
N(1)-C(2)-H(2)	114.0(14)	H(12B)-C(12)-H(12C)	109.5
C(3)-C(2)-H(2)	117.1(14)	C(5)-C(13)-C(15)	112.8(4)
Si(1)-C(2)-H(2)	122.0(14)	C(5)-C(13)-C(14)	111.3(4)
N(2)-C(3)-C(2)	102.5(2)	C(15)-C(13)-C(14)	108.6(4)
N(2)-C(3)-Si(1)	119.1(2)	C(5)-C(13)-H(13)	108.0
C(2)-C(3)-Si(1)	66.70(16)	C(15)-C(13)-H(13)	108.0
N(2)-C(3)-H(3)	116.8(17)	C(14)-C(13)-H(13)	108.0
C(2)-C(3)-H(3)	115.6(16)	C(13)-C(14)-H(14A)	109.5

Table 30 (con't).

Atoms	Angle	Atoms	Angle
C(13)-C(14)-H(14B)	109.5	C(22)-C(24)-H(24B)	109.5
H(14A)-C(14)-H(14B)	109.5	H(24A)-C(24)-H(24B)	109.5
C(13)-C(14)-H(14C)	109.5	C(22)-C(24)-H(24C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(24A)-C(24)-H(24C)	109.5
H(14B)-C(14)-H(14C)	109.5	H(24B)-C(24)-H(24C)	109.5
C(13)-C(15)-H(15A)	109.5	C(17)-C(25)-C(27)	110.9(4)
C(13)-C(15)-H(15B)	109.5	C(17)-C(25)-C(26)	112.5(3)
H(15A)-C(15)-H(15B)	109.5	C(27)-C(25)-C(26)	110.3(4)
C(13)-C(15)-H(15C)	109.5	C(17)-C(25)-H(25)	107.7
H(15A)-C(15)-H(15C)	109.5	C(27)-C(25)-H(25)	107.7
H(15B)-C(15)-H(15C)	109.5	C(26)-C(25)-H(25)	107.7
C(21)-C(16)-C(17)	122.4(3)	C(25)-C(26)-H(26A)	109.5
C(21)-C(16)-N(1)	119.2(3)	C(25)-C(26)-H(26B)	109.5
C(17)-C(16)-N(1)	118.4(3)	H(26A)-C(26)-H(26B)	109.5
C(16)-C(17)-C(18)	117.5(3)	C(25)-C(26)-H(26C)	109.5
C(16)-C(17)-C(25)	123.3(3)	H(26A)-C(26)-H(26C)	109.5
C(18)-C(17)-C(25)	119.2(3)	H(26B)-C(26)-H(26C)	109.5
C(19)-C(18)-C(17)	120.7(3)	C(25)-C(27)-H(27A)	109.5
C(19)-C(18)-H(18)	119.6	C(25)-C(27)-H(27B)	109.5
C(17)-C(18)-H(18)	119.6	H(27A)-C(27)-H(27B)	109.5
C(20)-C(19)-C(18)	121.1(3)	C(25)-C(27)-H(27C)	109.5
C(20)-C(19)-H(19)	119.5	H(27A)-C(27)-H(27C)	109.5
C(18)-C(19)-H(19)	119.5	H(27B)-C(27)-H(27C)	109.5
C(19)-C(20)-C(21)	121.5(3)	N(3)-C(28)-N(4)	104.4(2)
C(19)-C(20)-H(20)	119.2	N(3)-C(28)-Si(1)	124.2(2)
C(21)-C(20)-H(20)	119.2	N(4)-C(28)-Si(1)	131.3(2)
C(16)-C(21)-C(20)	116.8(3)	C(30)-C(29)-N(3)	107.6(3)
C(16)-C(21)-C(22)	123.3(3)	C(30)-C(29)-H(29)	126.2
C(20)-C(21)-C(22)	120.0(3)	N(3)-C(29)-H(29)	126.2
C(24)-C(22)-C(21)	111.3(3)	C(29)-C(30)-N(4)	107.0(3)
C(24)-C(22)-C(23)	111.8(4)	C(29)-C(30)-H(30)	126.5
C(21)-C(22)-C(23)	112.1(4)	N(4)-C(30)-H(30)	126.5
C(24)-C(22)-H(22)	107.1	C(36)-C(31)-C(32)	123.6(3)
C(21)-C(22)-H(22)	107.1	C(36)-C(31)-N(4)	119.7(3)
C(23)-C(22)-H(22)	107.1	C(32)-C(31)-N(4)	116.5(3)
C(22)-C(23)-H(23A)	109.5	C(33)-C(32)-C(31)	116.7(4)
C(22)-C(23)-H(23B)	109.5	C(33)-C(32)-C(40)	119.7(4)
H(23A)-C(23)-H(23B)	109.5	C(31)-C(32)-C(40)	123.6(3)
C(22)-C(23)-H(23C)	109.5	C(34)-C(33)-C(32)	121.0(5)
H(23A)-C(23)-H(23C)	109.5	C(34)-C(33)-H(33)	119.5
H(23B)-C(23)-H(23C)	109.5	C(32)-C(33)-H(33)	119.5
C(22)-C(24)-H(24A)	109.5	C(33)-C(34)-C(35)	121.4(5)

Table 30 (con't).

Atoms	Angle	Atoms	Angle
C(33)-C(34)-H(34)	119.3	C(32)-C(40)-C(42)	111.3(4)
C(35)-C(34)-H(34)	119.3	C(32)-C(40)-C(41)	111.0(4)
C(34)-C(35)-C(36)	120.9(5)	C(42)-C(40)-C(41)	111.2(4)
C(34)-C(35)-H(35)	119.5	C(32)-C(40)-H(40)	107.7
C(36)-C(35)-H(35)	119.5	C(42)-C(40)-H(40)	107.7
C(31)-C(36)-C(35)	116.3(4)	C(41)-C(40)-H(40)	107.7
C(31)-C(36)-C(37')	116.5(8)	C(40)-C(41)-H(41A)	109.5
C(35)-C(36)-C(37')	127.2(8)	C(40)-C(41)-H(41B)	109.5
C(31)-C(36)-C(37)	130.4(10)	H(41A)-C(41)-H(41B)	109.5
C(35)-C(36)-C(37)	113.0(10)	C(40)-C(41)-H(41C)	109.5
C(38)-C(37)-C(36)	108(2)	H(41A)-C(41)-H(41C)	109.5
C(38)-C(37)-C(39)	104.6(15)	H(41B)-C(41)-H(41C)	109.5
C(36)-C(37)-C(39)	102.7(12)	C(40)-C(42)-H(42A)	109.5
C(38)-C(37)-H(37)	113.6	C(40)-C(42)-H(42B)	109.5
C(36)-C(37)-H(37)	113.6	H(42A)-C(42)-H(42B)	109.5
C(39)-C(37)-H(37)	113.6	C(40)-C(42)-H(42C)	109.5
C(37)-C(38)-H(38A)	109.5	H(42A)-C(42)-H(42C)	109.5
C(37)-C(38)-H(38B)	109.5	H(42B)-C(42)-H(42C)	109.5
H(38A)-C(38)-H(38B)	109.5	C(44)-C(43)-C(48)	124.3(3)
C(37)-C(38)-H(38C)	109.5	C(44)-C(43)-N(3)	118.3(3)
H(38A)-C(38)-H(38C)	109.5	C(48)-C(43)-N(3)	117.3(3)
H(38B)-C(38)-H(38C)	109.5	C(43)-C(44)-C(45)	116.4(4)
C(37)-C(39)-H(39A)	109.5	C(43)-C(44)-C(52)	122.7(3)
C(37)-C(39)-H(39B)	109.5	C(45)-C(44)-C(52)	120.8(4)
H(39A)-C(39)-H(39B)	109.5	C(46)-C(45)-C(44)	120.5(4)
C(37)-C(39)-H(39C)	109.5	C(46)-C(45)-H(45)	119.8
H(39A)-C(39)-H(39C)	109.5	C(44)-C(45)-H(45)	119.8
H(39B)-C(39)-H(39C)	109.5	C(47)-C(46)-C(45)	121.4(4)
C(36)-C(37')-C(38')	118.4(16)	C(47)-C(46)-H(46)	119.3
C(36)-C(37')-C(39')	116.9(12)	C(45)-C(46)-H(46)	119.3
C(38')-C(37')-C(39')	105.4(12)	C(46)-C(47)-C(48)	121.0(4)
C(36)-C(37')-H(37')	104.9	C(46)-C(47)-H(47)	119.5
C(38')-C(37')-H(37')	104.9	C(48)-C(47)-H(47)	119.5
C(39')-C(37')-H(37')	104.9	C(47)-C(48)-C(43)	116.4(4)
C(37')-C(38')-H(38D)	109.5	C(47)-C(48)-C(49)	119.5(4)
C(37')-C(38')-H(38E)	109.5	C(43)-C(48)-C(49)	124.0(3)
H(38D)-C(38')-H(38E)	109.5	C(48)-C(49)-C(51)	111.9(4)
C(37')-C(38')-H(38F)	109.5	C(48)-C(49)-C(50)	112.9(4)
H(38D)-C(38')-H(38F)	109.5	C(51)-C(49)-C(50)	110.3(4)
H(38E)-C(38')-H(38F)	109.5	C(48)-C(49)-H(49)	107.1
C(37')-C(39')-H(39D)	109.5	C(51)-C(49)-H(49)	107.1
C(37')-C(39')-H(39E)	109.5	C(50)-C(49)-H(49)	107.1
H(39D)-C(39')-H(39E)	109.5	C(49)-C(50)-H(50A)	109.5
C(37')-C(39')-H(39F)	109.5	C(49)-C(50)-H(50B)	109.5
H(39D)-C(39')-H(39F)	109.5	H(50A)-C(50)-H(50B)	109.5
H(39E)-C(39')-H(39F)	109.5	C(49)-C(50)-H(50C)	109.5

Table 30 (con't).

Atoms	Angle	Atoms	Angle
H(50A)-C(50)-H(50C)	109.5	O(1)-C(55)-H(55A)	109.5
H(50B)-C(50)-H(50C)	109.5	O(1)-C(55)-H(55B)	109.5
C(49)-C(51)-H(51A)	109.5	H(55A)-C(55)-H(55B)	109.5
C(49)-C(51)-H(51B)	109.5	O(1)-C(55)-H(55C)	109.5
H(51A)-C(51)-H(51B)	109.5	H(55A)-C(55)-H(55C)	109.5
C(49)-C(51)-H(51C)	109.5	H(55B)-C(55)-H(55C)	109.5
H(51A)-C(51)-H(51C)	109.5	C(55)-O(1)-C(56)	100.1(9)
H(51B)-C(51)-H(51C)	109.5	C(57)-C(56)-O(1)	102.9(11)
C(44)-C(52)-C(54)	110.3(3)	C(57)-C(56)-H(56A)	111.2
C(44)-C(52)-C(53)	113.3(3)	O(1)-C(56)-H(56A)	111.2
C(54)-C(52)-C(53)	109.4(3)	C(57)-C(56)-H(56B)	111.2
C(44)-C(52)-H(52)	107.9	O(1)-C(56)-H(56B)	111.2
C(54)-C(52)-H(52)	107.9	H(56A)-C(56)-H(56B)	109.1
C(53)-C(52)-H(52)	107.9	O(2)-C(57)-C(56)	111.9(11)
C(52)-C(53)-H(53A)	109.5	O(2)-C(57)-H(57A)	109.2
C(52)-C(53)-H(53B)	109.5	C(56)-C(57)-H(57A)	109.2
H(53A)-C(53)-H(53B)	109.5	O(2)-C(57)-H(57B)	109.2
C(52)-C(53)-H(53C)	109.5	C(56)-C(57)-H(57B)	109.2
H(53A)-C(53)-H(53C)	109.5	H(57A)-C(57)-H(57B)	107.9
H(53B)-C(53)-H(53C)	109.5	C(57)-O(2)-C(58)	117.5(12)
C(52)-C(54)-H(54A)	109.5	O(2)-C(58)-H(58A)	109.5
C(52)-C(54)-H(54B)	109.5	O(2)-C(58)-H(58B)	109.5
H(54A)-C(54)-H(54B)	109.5	H(58A)-C(58)-H(58B)	109.5
C(52)-C(54)-H(54C)	109.5	O(2)-C(58)-H(58C)	109.5
H(54A)-C(54)-H(54C)	109.5	H(58A)-C(58)-H(58C)	109.5
H(54B)-C(54)-H(54C)	109.5	H(58B)-C(58)-H(58C)	109.5

APPENDIX B

RESEARCH PUBLICATIONS

Co-Authored by Mariham Abraham

1. Abraham, Mariham Y.; Wang, Yuzhong; Xie, Yaoming; Wei, Pingrong; Schaefer, III, Henry F.; Schleyer, Paul v. R.; Robinson, Gregory H. "Carbene Stabilization of Diarsenic – From Hypervalency to Allotropy" *Chem. Eur. J.* **2010**, 16, 432-435.
2. Wang, Yuzhong; Xie, Yaoming; Abraham, Mariham Y.; Gilliard Jr., Robert J.; Wei, Pingrong; Schaefer III, Henry F.; Schleyer, Paul v. R.; Robinson, Gregory H. "Carbene-Stabilized Parent Phosphinidene" *Organometallics* **2010**, 29, 4778-4780.
3. Wang, Yuzhong; Xie, Yaoming; Abraham, Mariham Y.; Wei, Pingrong; Schaefer, III, Henry F.; Schleyer, Paul v. R.; Robinson, Gregory H. "A Viable Anionic N-heterocyclic Dicarbene" *J. Am. Chem. Soc.* **2010**, 132, 14370-14372.
4. Wang, Yuzhong; Xie, Yaoming; Abraham, Mariham Y.; Wei, Pingrong; Schaefer, III, Henry F.; Schleyer, Paul v. R.; Robinson, Gregory H. "Carbene-Stabilized Diphosphorus: Bidentate Complexation of BH_2^+ " *Chem. Commun.* **2011**, 47, 9224-9226.
5. Wang, Yuzhong; Xie, Yaoming; Abraham, Mariham Y.; Wei, Pingrong; Schaefer, III, Henry F.; Schleyer, Paul v. R.; Robinson, Gregory H. "Anionic N-heterocyclic Dicarbene-Borane Binuclear Complexes" *Organometallics* **2011**, 30, 1303-1306.
6. Abraham, Mariham Y.; Wang, Yuzhong; Xie, Yaoming; Wei, Pingrong; Schaefer, III, Henry F.; Schleyer, Paul v. R.; Robinson, Gregory H. "Cleavage of Carbene-Stabilized Disilicon" *J. Am. Chem. Soc.* **2011**, 133, 8874-8876.
7. Wang, Yuzhong; Xie, Yaoming; Abraham, Mariham Y.; Gilliard Jr., Robert J.; Wei, Pingrong; Smith, Jared C.; Robinson, Gregory H. "From Anionic Dicarbene to Abnormal Carbene-Borane Complexes: A Logical Synthetic Route" *Organometallics* **2012**, 31, 791-793.
8. Abraham, Mariham Y.; Gilliard Jr., Robert J.; Smith, Jared C.; Wang, Yuzhong; Robinson, Gregory H. Inorganic Syntheses, Vol. 36: *m*-TERPHENYLGALLIUM CHLORIDE COMPLEXES. New York City, Hoboken. Wiley, **2012**.
9. Gilliard Jr., Robert J.; Abraham, Mariham Y.; Wang, Yuzhong; Wei, Pingrong; Xie, Yaoming; Quillian, Brandon; Schaefer III, Henry F.; Schleyer, Paul v. R.; Robinson, Gregory H. "Carbene-Stabilized Beryllium Borohydride" *J. Am. Chem. Soc.* **2012**, 134, 9953-9955.
10. Wang, Yuzhong; Xie, Yaoming; Abraham, Mariham Y.; Gilliard Jr., Robert J.; Wei, Pingrong; Schaefer III, Henry F.; Schleyer, Paul v. R.; Robinson, Gregory H. "NHC-

- Stabilized Triorganozincates: Syntheses, Structures, and Transformation to Abnormal Carbene-Zinc Complexes" *Angew. Chem., Int. Ed.* **2012**, 51, 10173-10176.
11. Abraham, Mariham Y.; Wang, Yuzhong; Xie, Yaoming; Gilliard Jr., Robert J.; Wei, Pingrong; Vaccaro, Brian J.; Johnson, Michael K.; Schaefer, III, Henry F.; Schleyer, Paul v. R.; Robinson, Gregory H. "Oxidation of Carbene-Stabilized Diarsenic: Diarsene Dications and Diarsenic Radical Cations" *J. Am. Chem. Soc.* **2013**, 135, 2486-2488.
 12. Wang, Yuzhong; Abraham, Mariham Y.; Gilliard Jr., Robert J.; Sexton, Daniel R.; Wei, Pingrong; Robinson, Gregory H. "N-Heterocyclic Olefin Stabilized Borenium Cations" *Organometallics* **2013**, DOI: 10.1021/om400539z.