

Electronic Thesis and Dissertation Repository

2-15-2018 2:15 PM

The Addition of Alkynes to Low-Valent Silicon Compounds: A Mechanistic Study

Andrew T. Henry, *The University of Western Ontario*

Supervisor: Baines, Kim M., *The University of Western Ontario*

A thesis submitted in partial fulfillment of the requirements for the Master of Science degree in Chemistry

© Andrew T. Henry 2018

Follow this and additional works at: <https://ir.lib.uwo.ca/etd>

 Part of the [Inorganic Chemistry Commons](#)

Recommended Citation

Henry, Andrew T., "The Addition of Alkynes to Low-Valent Silicon Compounds: A Mechanistic Study" (2018). *Electronic Thesis and Dissertation Repository*. 5202.
<https://ir.lib.uwo.ca/etd/5202>

This Dissertation/Thesis is brought to you for free and open access by Scholarship@Western. It has been accepted for inclusion in Electronic Thesis and Dissertation Repository by an authorized administrator of Scholarship@Western. For more information, please contact wlsadmin@uwo.ca.

Abstract

The mechanism for the addition of alkynes to low-valent silicon compounds was investigated in this thesis using a cyclopropyl alkyne mechanistic probe **1.31** ((2-ethynyl-3-methoxy-1-methylcyclopropyl)benzene). The addition of alkyne **1.31** to the asymmetrically-substituted disilene **1.37** ($\text{Tip}_2\text{Si}=\text{SiTipPh}$) was investigated. The structures of the products obtained indicate the reaction proceeds through a stepwise mechanism with a biradical intermediate and the dipole moment of the disilene bond was not sufficient to alter the reaction mechanism.

The addition of alkyne **1.31** to the NHC-stabilized silylene **1.38** (${}^t\text{Bu}_3\text{Si}(\text{H})\text{Si}\leftarrow\text{NHC}$) was also investigated. The structure of the product formed in the reaction lead to two conclusions: that silylene **1.38** acts as a nucleophile in the reaction with alkyne **1.31**, and the cyclopropyl ring of alkyne **1.31** regioselectively opens toward the phenyl substituent in the presence of an α -anion.

Keywords: low-valent, silicon, disilene, silylene, alkyne, cycloaddition, mechanistic probe, cyclopropyl

Acknowledgments

First and foremost, big thanks to my supervisor, Dr. Kim Baines. She has provided guidance throughout my time in her research group. Her knowledge has helped me overcome several obstacles in my research project. She has also provided me various skills to become a better researcher. She always pushed me to “see the big picture” with my research and helped me regain confidence when my projects were not working out. Her numerous edits to my thesis were done in a manner not only to correct my work but have me learn to properly communicate my thoughts in my writing. I can’t wait to continue my time in your research group for my Ph.D.

Secondly, I would like to thank Jeremy, Mike, Bahar, and Nada who mentored me during the course of my thesis. You always listened to my stupid questions and provided guidance in my research when I needed it. You provided an outlet to discuss our chemistry and I learned so much from you guys. Next, I need to thank the remaining members, Sarah and Maissa, aka the “Lit Squad”. You, along with the undergrads (Robert, Curtis and Courtney), really connected the Baines group together. From reading our horoscopes in the Tim’s line, to the Sporcle quizzes during our lunch breaks, to all the celebrations in the office, you guys continue to trigger me bring a smile to my face. I look forward to continuing my chemistry journey with you guys in May.

I’d also like to thank the staff at Western. There’s so many of you to thank for keeping this department running. Special thanks go to Mat Willans and Doug Hairsine for their NMR and MS expertise.

Finally, thanks to all the friends I've made at Western over my time here. All the parties and times at the grad club have been a blast. Special shout outs to my lunch "support group", Hendrick Chan and Scott Hendrix (and James, Cam, Ben, and Jonathan on occasion) who provided a space to vent about any problems, whether it was chemistry related or not. Also, shout out to the Blacquiere group who have always helped me when I needed it.

Table of Contents

Abstract.....	i
Acknowledgments.....	ii
Table of Contents.....	iv
List of Tables.....	vi
List of Figures.....	vii
List of Schemes.....	ix
List of Charts.....	xiii
List of Appendices.....	xiv
List of Abbreviations.....	xv
Chapter 1.....	1
1 General Introduction.....	1
1.1 History of Alkyne Cycloaddition to Disilenes and Silylenes.....	1
1.2 Applications of Alkyne Cycloaddition Reactions in Disilene and Silylene Chemistry.....	7
1.3 Mechanistic Overview.....	11
1.4 Project Overview.....	20
1.5 References.....	23
Chapter 2.....	28
2 Investigation into the Mechanism of the Addition of a Cyclopropyl Alkyne to an Asymmetrical Disilene.....	28
2.1 Introduction.....	28
2.2 Results and Discussion.....	33
2.2.1 Structure Elucidation.....	33
2.2.2 Mechanistic Insights.....	54
2.3 Conclusions.....	58

2.4	Experimental	60
2.4.1	General Procedure.....	60
2.4.2	Addition of Probe 1.31 to Asymmetric Disilene 1.37	60
2.5	References.....	68
Chapter 3.....		70
3	Investigation into the Mechanism of the Addition Alkynes to an NHC-Stabilized Silylene.....	70
3.1	Introduction.....	70
3.2	Results and Discussion	79
3.2.1	Structure Elucidation	79
3.2.2	Mechanistic Insights	86
3.3	Conclusions.....	91
3.4	Experimental	92
3.4.1	General Procedure.....	92
3.4.2	Addition of Alkyne 1.31 to Silylene 1.38	93
3.5	References.....	95
Chapter 4.....		98
4	Conclusions and Future Work.....	98
4.1	Summary and Conclusions	98
4.2	Future Work	103
4.3	References.....	105
Appendices.....		106
Curriculum Vitae		109

List of Tables

Table 1.1: Summary of mechanistic pathways of the reactions between (di)tetrelenes with alkyne 1.31.....	17
Table 2.1: ^1H NMR and ^{13}C NMR chemical shifts of 2.5, 2.6, 2.10, and 2.11.....	35
Table 2.2: ^1H NMR and ^{13}C NMR chemical shifts of 2.7, 2.12, and 2.13.	48
Table 2.3: $^3J_{\text{Si-H}}$ coupling constants for known disilacyclobutene compounds	52
Table 2.4: Literature reported nucleophile-specific parameters for various alkynes and NHC compounds.	56
Table 2.5: Summary of Structural Parameters for 2.10.	63
Table 3.1: ^{13}C - ^1H HMBC correlations utilized in elucidating the core structure of 3.20.....	83
Table 3.2: ^1H , ^{13}C , and ^{29}Si chemical shifts for 3.20 and 1.39.	85

List of Figures

Figure 1.1: The two different orientations of orbital overlap between silylene and the π -orbitals of an alkyne	19
Figure 2.1: a) ^1H NMR spectrum (600 MHz, C_6D_6) of 2.10; b) Expansion from 6.70 – 7.12 ppm; c) Expansion from 3.8-5.0 ppm.	36
Figure 2.2: Expansion of the ^{13}C - ^1H gHMBC NMR spectrum of 2.10 (600 MHz, C_6D_6) with ^1H ranges of: a) 4.40-5.00 ppm; b) 3.85-4.75 ppm; c) 4.85-5.05 ppm; d) 2.12-2.26 ppm.	37
Figure 2.3: Expansion of the ^{29}Si - ^1H gHMBC NMR spectrum of 2.10 (600 MHz, C_6D_6). The signals at -32 and -12 ppm in the ^{29}Si dimension are noted as Si(1) and Si(2) respectively. .	39
Figure 2.4: Ellipsoid plot of 2.10 showing naming and numbering scheme. Ellipsoids are at the 50% probability level, all ligand-based hydrogen atoms and Tip groups (except the <i>i</i> -carbon) were omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Si1-Si2 = 2.4795(10), C4-C5 = 1.345(4), C3-C13 = 1.340(4), Si1-Si2-C5 = 97.21(8), Si2-C5-C4 = 136.4(2), C5-C4-C3 = 129.9(3), C4-C3-C2 = 120.8(2), C3-C2-C1 = 115.1(2), C2-C1-Si1 = 117.05(16), C1-Si1-Si2 = 102.07(7).	41
Figure 2.5: a) ^1H NMR spectrum of 2.11 (600 MHz, C_6D_6); b) Expansion from 6.69 – 6.71 ppm; c) Expansion from 3.6 – 4.1 ppm; d) Expansion from 1.30 – 1.35 ppm.	42
Figure 2.6: Expansion of the ^{13}C - ^1H gHMBC NMR spectrum of 2.11 (600 MHz, C_6D_6) with ^1H ranges of: a) 3.00-4.10 ppm; b) 3.60-3.80 ppm (^{13}C range of 17.5-18.0 ppm); c) 3.60-3.80 ppm (^{13}C range of 218.0-218.6 ppm);.....	43
Figure 2.7: Expansion of the ^{29}Si - ^1H gHMBC NMR spectrum of 2.11 (600 MHz, C_6D_6). The signals at -31 and -28 ppm in the ^{29}Si dimension are noted as Si(1) and Si(2), respectively.	45
Figure 2.8: a) ^1H NMR spectrum of 2.12 (600 MHz, C_6D_6); b) Expansion from 3.56 – 3.64 ppm; c) Expansion from 2.80 – 2.90 ppm.	47

Figure 2.9: Expansion of the ^{13}C - ^1H gHMBC NMR spectrum of 2.12 (600 MHz, C_6D_6) with ^1H ranges of: a) 7.38-7.50 ppm (^{13}C range of 36.5-37.5 ppm); b) 1.17-1.31 ppm (^{13}C range of 36.5-37.5 ppm); c) 1.0-7.5 ppm (^{13}C range of 176.0-178.0 ppm); 49

Figure 2.10: Expansion of the ^{29}Si - ^1H gHMBC NMR spectrum of 2.12 (600 MHz, C_6D_6). The signals at -16 and -12 ppm in the ^{29}Si dimension are noted as Si(1) and Si(2), respectively. 50

Figure 3.1: ^1H NMR spectrum of 3.20 (C_6D_6 , 600 MHz). Expansions from a) 1.9-6.9 ppm b) 5.31-5.43 ppm c) 2.98-3.06 ppm d) 2.39-2.45 ppm e) 6.75-6.89 ppm. 80

Figure 3.2: Expansion of the ^{29}Si - ^1H gHMBC NMR spectrum of 3.20 (600 MHz, C_6D_6) with ^1H ranges of: a) 5.25-5.60 ppm; b) 2.00-3.40 ppm; c) 6.65-6.90 ppm; d) 0.8-1.4 ppm. 81

Figure 3.3: Expansion of the ^{13}C - ^1H gHMBC NMR spectrum of 3.20 between 2.0-7.0 ppm in the ^1H dimension and 135.0-151.0 in the ^{13}C dimension (600 MHz, C_6D_6)..... 83

List of Schemes

Scheme 1.1: General reactions of trapping agents with a transient disilene and the observed products.....	2
Scheme 1.2: Reaction of transient disilene 1.2 with diphenylacetylene and phenyltrimethylsilylacetylene.	2
Scheme 1.3: Addition of alkynes to tetramesityldisilene 1.4.....	3
Scheme 1.4: Addition of phenylacetylene to disilene 1.5.....	3
Scheme 1.5: Products observed in the addition of acetylenes to transient silylenes.	4
Scheme 1.6: Formation of the transient silylene 1.6 and reaction with diphenylacetylene and 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne.	4
Scheme 1.7: Thermolysis of 1.8 to give 1.9 and 1.10.....	5
Scheme 1.8: Thermolysis of 1.11 yielding disilacyclobutenes 1.12 and siloles 1.13 and 1.14.	5
Scheme 1.9: Addition of phenylacetylene and diphenylacetylene to silylene 1.15.....	6
Scheme 1.10: Cycloaddition of NHC-stabilized silylene 1.17 with bis(dimethylamino)acetylene and bis(diethylamino)acetylene to form silole 1.16.....	7
Scheme 1.11: Formation of the surface adduct between the Si(100) 2x1 surface and buta-1,3-diyne.....	8
Scheme 1.12: Oligomerization by cycloaddition between bifunctional monomers containing disilene and alkyne moieties.	9
Scheme 1.13: Nitrile insertion into a silacyclopropene.	9
Scheme 1.14: Illustration of the symmetry forbidden $[2\pi_s+2\pi_s]$ cycloaddition of two alkenes.	11

Scheme 1.15: Stepwise addition of diphenylacetylene to 1.22.....	12
Scheme 1.16: Reaction of disilene 1.25 with phenylacetylene and ethoxyacetylene.....	13
Scheme 1.17: Reaction of disilene 1.4 with various alkynes.....	14
Scheme 1.18: Stepwise addition of various polar acetylenes forming a zwitterionic intermediate.....	14
Scheme 1.19: Reactivity of 1.31, under radical and cationic conditions.....	15
Scheme 1.20: Formation of disilacyclobutene 1.33 and disilacyclohepta-3,4-diene 1.32 from the reaction of disilenes with alkyne 1.31.....	16
Scheme 1.21: Potential pathways for the formation of 1,4-disilahexadiene 1.35.....	18
Scheme 1.22: Generation of transient silylene 1.36 and subsequent addition of various acetylenes.....	20
Scheme 1.23: Addition of phenylacetylene to 1.5 and 1.37. Chapter 2 examines the addition of 1.31 to 1.37.....	21
Scheme 1.24: Addition of diphenylacetylene to silylene 1.38. Chapter 3 examines the addition of 1.31 to 1.38.....	22
Scheme 2.1: Polymerization of the linker bridged tetrasiladiene 1.18 with 1,4-diethynyl benzene.....	28
Scheme 2.2: Cycloaddition of phenylacetylene to asymmetrically-substituted disilenes 1.37 and 1.5, and the symmetrically substituted 1.4.....	29
Scheme 2.3: Reaction of a donor NHC with the asymmetric disilene moiety in 2.3.....	30
Scheme 2.4: Regioselective ring opening of cyclopropyl alkyne probe 1.31 upon addition of a radical or a cation.....	31
Scheme 2.5: Reaction of tetramesityldisilene 1.4 with alkyne 1.31.....	31

Scheme 2.6: Mechanism for the addition of probe 1.31 to tetramesityldisilene 1.4.....	32
Scheme 2.7: The addition of alkyne 1.31 to 1.37 yielding two stereoisomers.	53
Scheme 2.8: The reaction of disilene 1.31 with alkyne 1.37.	54
Scheme 2.9: Mechanism of the reaction between cyclopropyl alkyne probe 1.31 and 1.37..	55
Scheme 2.10: Addition of phenylacetylene and ethoxyacetylene to silene 2.16.	57
Scheme 2.11: Addition of phenylacetylene and ethoxyacetylene to germene 2.19.....	58
Scheme 3.1: Synthesis of stable Lewis base-stabilized silylenes 3.3.	71
Scheme 3.2: Synthesis of the first NHC-stabilized silylenes 3.5 and 3.6.	72
Scheme 3.3: Generation of transient silylene 1.36 and subsequent addition of various acetylenes.....	73
Scheme 3.4: Addition of diphenylacetylene to NHC-stabilized silylene 3.7.	73
Scheme 3.5: The reaction between bis(amino)acetylenes and silylene 3.9.	74
Scheme 3.6: Proposed mechanisms for the formation of 3.10.	74
Scheme 3.7: Reaction of phenylacetylene and diphenylacetylene with silylene 1.38.....	75
Scheme 3.8: The favoured pathway to silole 1.39.	76
Scheme 3.9: Addition of phenylacetylene to silylene 3.15 and the proposed zwitterionic intermediate.....	76
Scheme 3.10: Addition of an internal alkyne to silylene 3.15.	77
Scheme 3.11: The regioselectivity of cyclopropyl ring opening.	78
Scheme 3.12: The reaction of silylene 1.38 with alkyne 1.31.	86
Scheme 3.13: The proposed mechanism for the formation of 3.20.	87

Scheme 3.14: Reaction of 3.25 with butyllithium.	89
Scheme 3.15: Mechanism for the addition of cyclopropyl probe 1.31 to tetramesityldigermene 3.28.....	90
Scheme 3.16: Addition of methanol to a silene.	90
Scheme 4.1: Reaction of disilene 1.37 with 1.31.....	99
Scheme 4.2: Mechanism of the reaction between cyclopropyl alkyne 1.31 and disilene 1.37.	100
Scheme 4.3: Reaction of 1.38 with 1.31.	101
Scheme 4.4: The proposed mechanism for the formation of 3.20.	102
Scheme 4.5: The proposed reactivity between the polar disilene 4.1 and alkyne 1.31.	104
Scheme 4.6: Possible reaction pathways of a simple silylene with alkyne 1.31.	104

List of Charts

Chart 1.1: 1.20, a silole that exhibits AIE.	10
Chart 2.1: Fragments of 2.10 highlighting key ^1H signals in blue.....	37
Chart 2.2: Elucidated structure for 2.10 highlighting key ^1H signals in blue.	40
Chart 2.3: Fragments of 2.11 highlighting key ^1H signals in blue and key ^{13}C signals in red.	44
Chart 2.4: Elucidated structure of 2.11 highlighting key ^{29}Si signals in green.....	46
Chart 2.5: Elucidated structure for 2.12.....	52
Chart 3.1: Representation of a Lewis-base stabilized silylene.	71
Chart 3.2: Fragment of 3.20 based on correlations in the ^{29}Si - ^1H gHMBC and ^1H - ^1H gCOSY NMR spectra.	82
Chart 3.3: Fragment of 3.20 with silole ring ^1H and ^{13}C chemical shifts listed.....	84
Chart 3.4: The final elucidated structure for 3.20.....	86
Chart 3.5: Comparison of the structure of 3.21 with the analogous zwitterionic intermediates proposed by Inoue and Cui.	88

List of Appendices

Appendix A1.1: ^{13}C NMR spectrum (119 MHz, C_6D_6) of 2.10.	106
Appendix A1.2: ^{13}C NMR spectrum (119 MHz, C_6D_6) of 2.11.	106
Appendix A1.3: ^{13}C NMR spectrum (119 MHz, C_6D_6) of 2.12.	107
Appendix A1.4: ^1H NMR spectrum (600 MHz, C_6D_6) of 2.13.	107
Appendix A1.5: ^{13}C NMR spectrum (119 MHz, C_6D_6) of 2.13.	108
Appendix A1.6: ^{13}C NMR spectrum (119 MHz, C_6D_6) of 3.20.	108

List of Abbreviations

°	degrees
Å	Ångström
AIE	aggregation-induced emission
Ar	Aryl group
br	broad
Bu	butyl
calcd	calculated
Cp*	1,2,3,4,5-Pentamethylcyclopentadiene
d	doublet
DCM	dichloromethane
DFT	density functional theory
Dip	2,6-diisopropylphenyl
ESI	electrospray ionization
Et	ethyl
EtOAc	ethyl acetate
gCOSY	correlation spectroscopy
gHMBC	gradient heteronuclear multiple bond coherence
gHSQC	gradient heteronuclear multiple quantum coherence
h	hour
HOMO	highest occupied molecular orbital
<i>i</i> Pr	<i>Iso</i> -propyl
LUMO	lowest occupied molecular orbital
<i>m/z</i>	mass to charge ratio
m	multiplet

<i>m</i>	meta
Me	methyl
Mes	2,4,6-trimethylphenyl
Mes*	2,4,6-tritertbutylphenyl
mg	milligram
MHz	megahertz
mL	millilitre
mmol	millimols
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
<i>o</i>	ortho
<i>p</i>	para
Ph	phenyl
ppm	parts per million
q	quartet
R	organic substituent
RT	room temperature
s	singlet
sept	septet
t	triplet
<i>t</i> Bu	<i>tert</i> -butyl
Tbt	2,4,6-tris[bis(trimethylsilyl)methyl]phenyl
THF	tetrahydrofuran
Tip	2,4,6-triisopropylphenyl
TLC	thin layer chromatography

TMOP	2,4,6-trimethoxyphenyl
TOF	time of flight
X	halide, or halogen

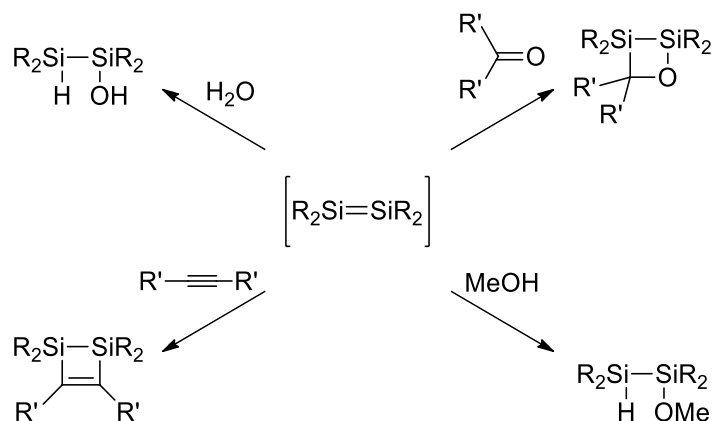
Chapter 1

1 General Introduction

1.1 History of Alkyne Cycloaddition to Disilenes and Silylenes

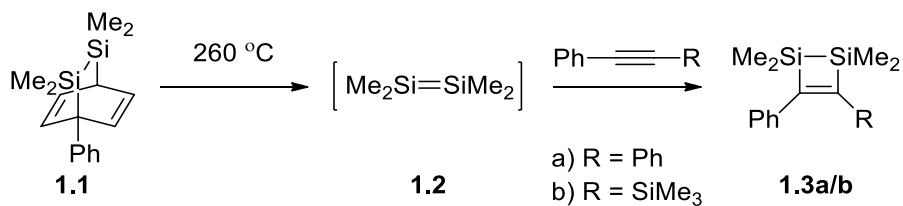
For the past half century, the chemistry of low-valent silicon compounds has been extensively studied.¹ Specifically, disilenes and silylenes, the silicon analogues of alkenes and carbenes respectively, have been shown to undergo many cycloaddition reactions under ambient conditions. When disilenes and silylenes are reacted with alkynes, they yield a complex ring system in a clean, high-yielding one pot reaction. As such, the reactivity of low-valent silicon compounds with alkynes has been a key focus of research.

One of the common methods for providing evidence for the formation of transient disilene and silylene species is to react the transient species with a trapping agent, a species that reacts cleanly and in high yield with the unsaturated silicon species. While typical trapping agents such as water, methanol, and ketones are often utilized² (Scheme 1.1), alkynes are also commonly employed to provide indirect evidence for the transient species.



Scheme 1.1: General reactions of trapping agents with a transient disilene and the observed products

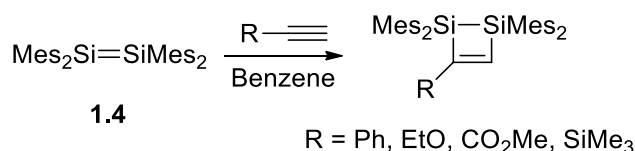
For example, when the bicycle **1.1** was heated, decomposition was observed.³ One of the decomposition products was proposed to result from oligomerization of disilene **1.2**. Upon co-pyrolysis of **1.1** with phenyltrimethylsilylacetylene or diphenylacetylene, disilacyclobutenes **1.3** were formed (Scheme 1.2).⁴



Scheme 1.2: Reaction of transient disilene **1.2** with diphenylacetylene and phenyltrimethylsilylacetylene.

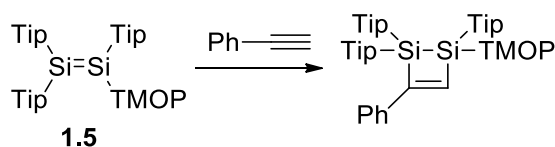
With the discovery of stable, isolable disilenes⁵ and silylenes,⁶ the reaction with alkynes continued to be one of the first reactions explored in studies of the reactivity of

these compounds. The first stable, isolable disilene, tetramesityldisilene **1.4**, was reacted with various alkynes yielding disilacyclobutenes (Scheme 1.3).⁷ This study confirmed that the addition of alkynes to disilenes provides a reliable, clean route to disilacyclobutenes under mild conditions.



Scheme 1.3: Addition of alkynes to tetramesityldisilene **1.4**.

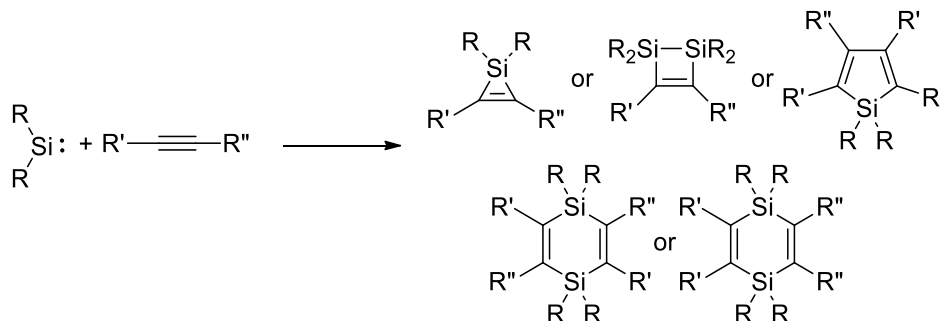
The cycloaddition of alkynes continues to be a key reaction examined upon the synthesis of a new disilene. For example, in 2013, Scheschkewitz reported the synthesis of disilene **1.5**, with three 2,4,6-triisopropylphenyl (Tip) substituents and the novel 2,4,6-trimethoxyphenyl (TMOP) protecting group.⁸ One of the first reactions examined was the reaction of **1.5** with phenylacetylene which afforded a disilacyclobutene. Interestingly, the addition of phenylacetylene was regioselective to the less hindered silicon.



Scheme 1.4: Addition of phenylacetylene to disilene **1.5**.

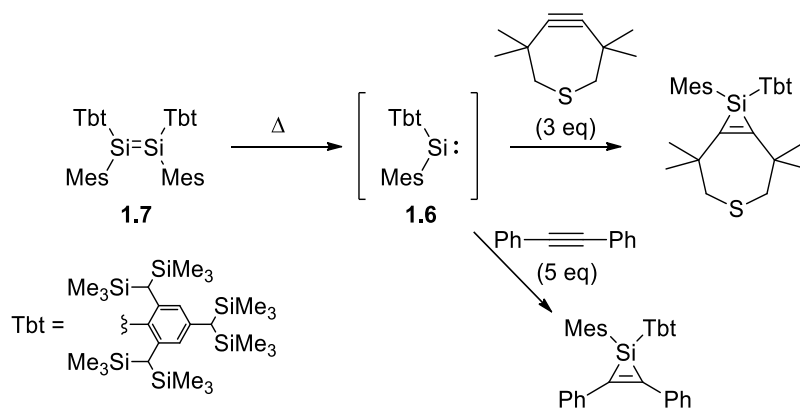
While disilenes typically afford a disilacyclobutene as the only product upon reaction with an alkyne; except in rare cases,⁹ silylenes give various products.

Specifically, the addition of alkynes to transient silylenes afford silacyclopropenes, disilacyclobutenes, 1,4-disila-2,5-dienes, and/or siloles (Scheme 1.5).¹⁰



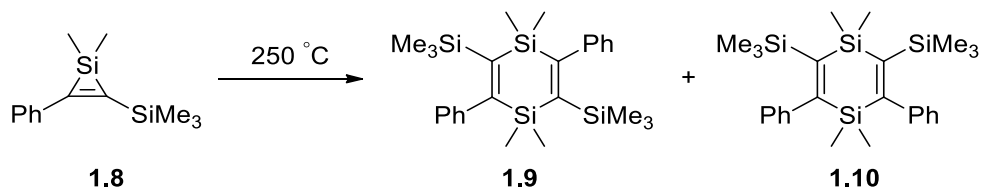
Scheme 1.5: Products observed in the addition of acetylenes to transient silylenes.

For example, the transient silylene **1.6**, generated by thermolysis of disilene **1.7** at 70 °C, reacted with 1,2-diphenylacetylene or 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne to give, in both cases, a silacyclopropene (Scheme 1.6).¹¹



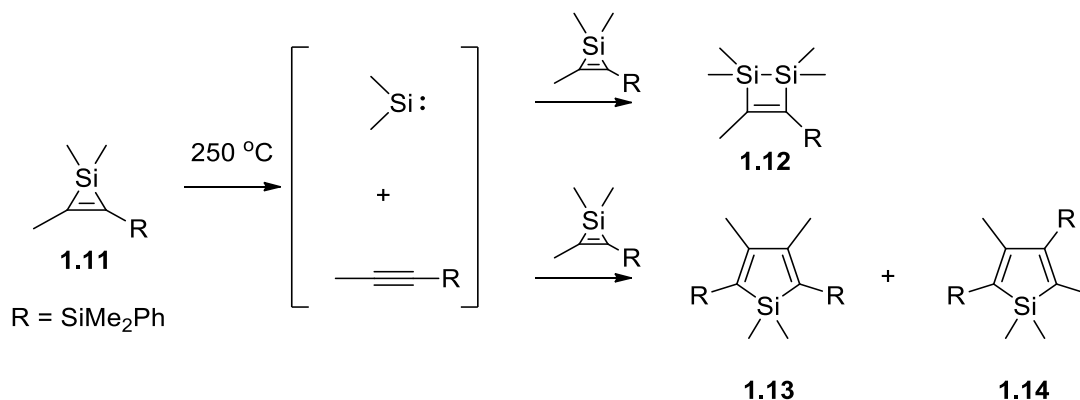
Scheme 1.6: Formation of the transient silylene **1.6** and reaction with diphenylacetylene and 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne.

In cases where the silacyclopropenes are not stabilized by the steric bulk of the ligands they can react further. For example, thermolysis of silacyclopropene **1.8** at 250 °C afforded the dimerized 1,4-disilacyclohex-2,5-enes **1.9** and **1.10** (Scheme 1.7).¹²



Scheme 1.7: Thermolysis of **1.8** to give **1.9** and **1.10**.

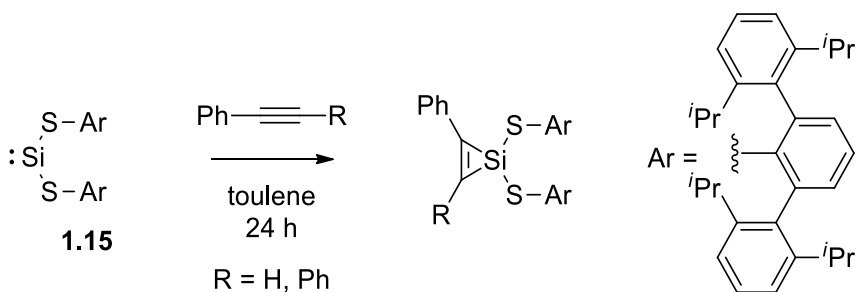
Thermolysis of **1.11** gave three products: disilacyclobutene **1.12** and two isomers of a silole, **1.13** and **1.14** (Scheme 1.8).¹³ Presumably, thermal decomposition of silacyclopropene **1.11** produces an equivalent of dimethylsilylene and 1-(dimethylphenylsilyl)propyne. The silylene then inserts into another equivalent of silacyclopropene **1.11** to form **1.12** or insert into another equivalent of the alkyne to afford the isomeric **1.13** and **1.14**.



Scheme 1.8: Thermolysis of **1.11** yielding disilacyclobutenes **1.12** and siloles **1.13** and **1.14**.

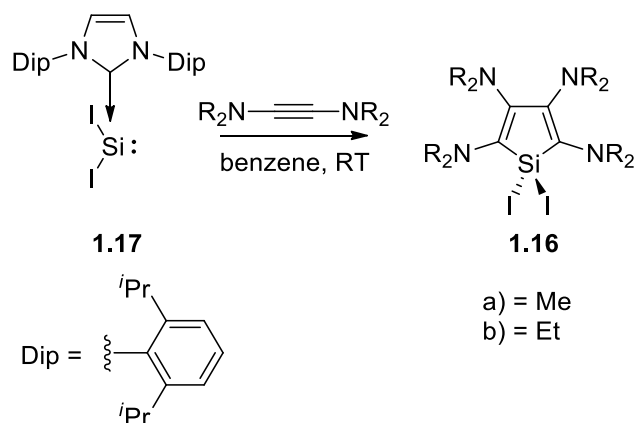
While the addition of an alkyne to a silylene generates a silacyclopropene, the previous two examples illustrate that the secondary products, disilacyclobutenes, siloles, and 1,4-disilacyclohex-2,5-enes are derived from further reactivity of the silacyclopropene.

The types of products formed upon the reaction of stable silylenes with alkynes is less varied in comparison to the more reactive transient species, giving, in general, silacyclopropenes. For example, Power reported that the stable silylene, **1.15**, reacts with phenylacetylene and diphenylacetylene to afford a silacyclopropene (Scheme 1.9).¹⁴



Scheme 1.9: Addition of phenylacetylene and diphenylacetylene to silylene **1.15**.

Silylenes can also be stabilized by the coordination of Lewis bases. While there are limited studies of the reactivity of Lewis base stabilized silylenes, the reaction with alkynes does not, in general, give a silacyclopropene. Instead, a silole is the most commonly observed product from the reaction. An example is silole **1.16** synthesized from the reaction of bis(dimethylamino)acetylene and the diethylamino derivative with the N-heterocyclic carbene (NHC) stabilized silylene **1.17**, as reported by Filippou (Scheme 1.10).¹⁵



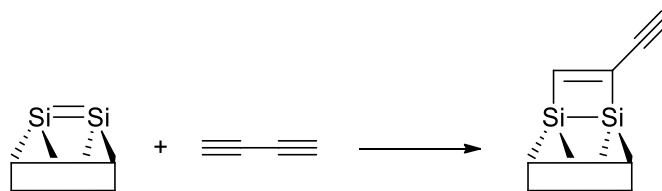
Scheme 1.10: Cycloaddition of NHC-stabilized silylene **1.17** with bis(dimethylamino)acetylene and bis(diethylamino)acetylene to form silole **1.16**.

1.2 Applications of Alkyne Cycloaddition Reactions in Disilene and Silylene Chemistry

The cycloaddition of alkynes to disilenes and silylenes features prominently in a variety of applications. The addition of alkynes to disilenes has been utilized to functionalize silicon dimers on surfaces and in the synthesis of organic-inorganic silicon hybrid polymers. Silacycloprenes, derived from the reaction of alkynes with silylenes, are utilized as building blocks in the synthesis of a variety of silicon-containing heterocycles. The electronic properties of siloles make them promising components of solar cells and other electronic devices. Herein, the applications are described.

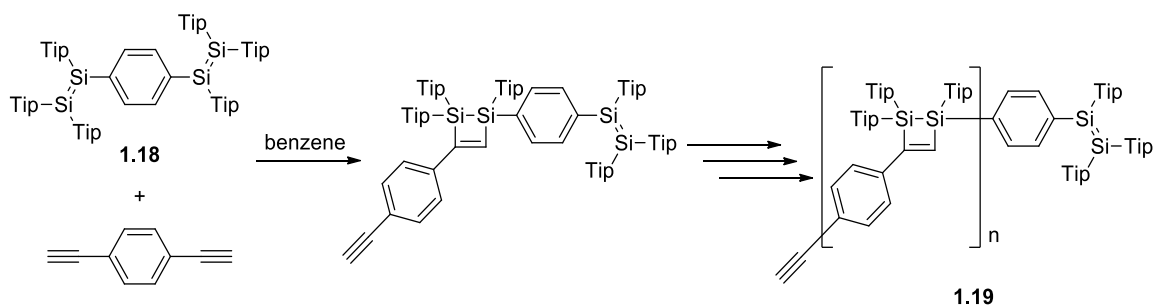
There is much interest in the organic functionalization of silicon surfaces for applications in electronics.¹⁶ As such, understanding the reactivity of these silicon surfaces is crucial. Reconstructed Si(100) 2×1 surfaces feature rows of silicon dimer units

which are separated by trenches and react similarly to the molecular dimeric analogues. One approach to understand the reactivity of the silicon surface dimers is to employ a molecular disilene as a model system. Multiple studies on the functionalization of the reconstructed surfaces have been conducted.¹⁷ For example, the addition of acetylene to the Si(100) 2×1 surface generates a disilacyclobutene similar to the molecular system.¹⁸ Buta-1,3-diyne also reacts with the Si(100) 2×1 surface (Scheme 1.11);¹⁹ albeit through only one alkyne unit. The remaining alkynyl group potentially enables the addition of a secondary organic layer to the silicon surface by the reaction with the alkyne moiety.



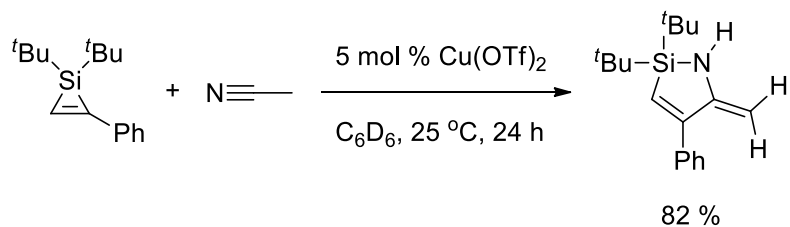
Scheme 1.11: Formation of the surface adduct between the Si(100) 2x1 surface and buta-1,3-diyne

The cycloaddition of alkynes to disilenes has also been utilized as the key bond-forming reaction in the synthesis of organic-inorganic silicon hybrid polymers.²⁰ The reaction between the bifunctional phenylene-bridged (bis)disilene **1.18** and 1,4-diethynyl benzene leads to the formation of the organic-inorganic hybrid polymer **1.19** (Scheme 1.12).



Scheme 1.12: Oligomerization by cycloaddition between bifunctional monomers containing disilene and alkyne moieties.

Silacyclopropenes, the product of the reaction between silylenes and alkynes, have been shown to undergo various insertion reactions, making silacyclopropenes a good precursor to many silicon-containing heterocycles.²¹ Transition metals have often been utilized to catalyze silacyclopropene insertion reactions. For example, the copper-catalyzed insertion of aldehydes²² or nitriles (Scheme 1.13)²³ are high-yielding routes to oxasilacyclopentenes and azasilacyclopentadienes, respectively. The former can be converted into 1,2,4-triols, while the latter can be converted to allylic amines which are useful building blocks for organic synthesis.²⁴



Scheme 1.13: Nitrile insertion into a silacyclopropene.

In another example, the palladium-catalyzed insertion of alkynes into the Si-C bond of a silacyclopene is a high-yielding, selective route to siloles.²⁵ Siloles, due to their conjugated electronic structures, have been utilized as luminogenic materials. While the photoemission of most conventional chromophores is quenched upon aggregation, hampering their practical applications, siloles exhibit aggregation-induced emission (AIE), fluorescing strongly in the aggregated state.²⁶ AIE, combined with their stability and good solubility in organic solvents, make siloles such as **1.20**, interesting photoelectronic materials (Chart 1.1).

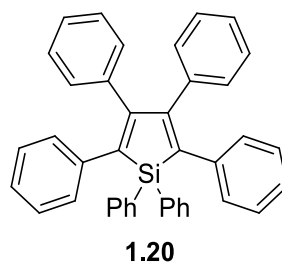
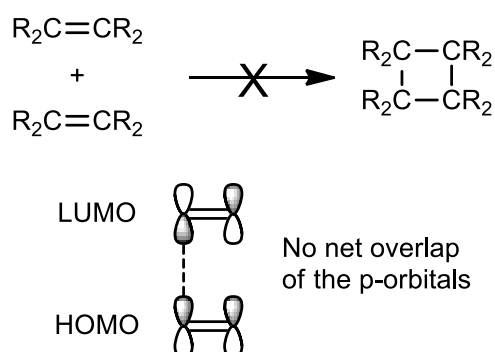


Chart 1.1: **1.20**, a silole that exhibits AIE.

Similarly, 1,4-disilacyclohex-2,5-enes, the dimers of silacycloprenes, exhibit cross-hyperconjugation which can be tuned to influence their optical and electronic properties for specialty applications.²⁷

1.3 Mechanistic Overview

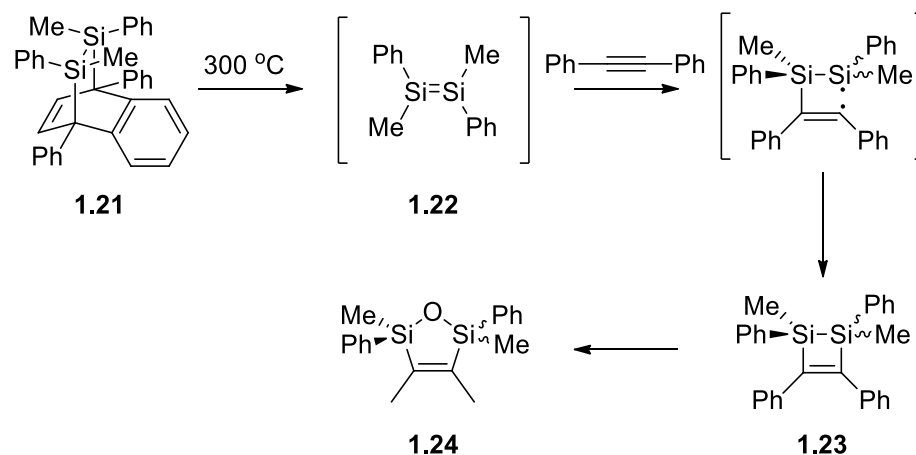
Given the importance of the cycloaddition of alkynes to low-valent silicon compounds, it is critical that the mechanism of the reaction be understood. The $[2\pi_s+2\pi_s]$ cycloaddition of alkynes and alkenes is forbidden by symmetry (Scheme 1.14),²⁸ and thus, the facile reactivity of disilenes with alkynes is in stark contrast to their lighter congeners.



Scheme 1.14: Illustration of the symmetry forbidden $[2\pi_s+2\pi_s]$ cycloaddition of two alkenes.

The mechanism of the addition of alkynes to disilenes has been debated since its discovery. In 1985, Sakurai provided the first mechanistic insight into this reaction.²⁹ Pyrolysis of the bicyclic compound **1.21**, with the substituents at silicon in the *trans* orientation, is known to produce the *trans* disilene **1.22** stereoselectively.³⁰ The stereochemistry of the substituents at silicon in disilacyclobutenes **1.23**, derived from the reaction with diphenylacetylene, was inferred after stereoselective oxidation to **1.24**. A 63:37 ratio of the *trans* and *cis* stereoisomers of **1.24**, respectively, were isolated by thin

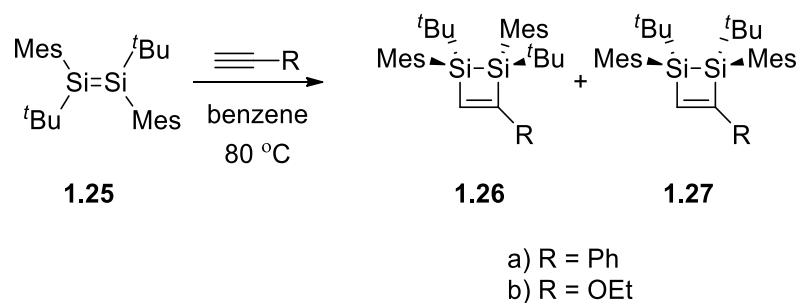
layer chromatography (TLC). The same reaction was also performed with the *cis* isomer of **1.21** and yielded a 38:62 ratio of *trans* and *cis* stereoisomers of **1.24**, respectively, demonstrating the reaction was stereoselective, but not stereospecific. Sakurai proposed that the reaction proceeds by a stepwise mechanism involving a biradical intermediate where the stereochemistry can be altered by Si-Si bond rotation or inversion of the silyl radical center (Scheme 1.15). The stereoselectivity of the reaction suggests that the scrambling of the stereochemistry, while competitive, is slower than ring closure forming the disilacyclobutene ring.



Scheme 1.15: Stepwise addition of diphenylacetylene to **1.22**.

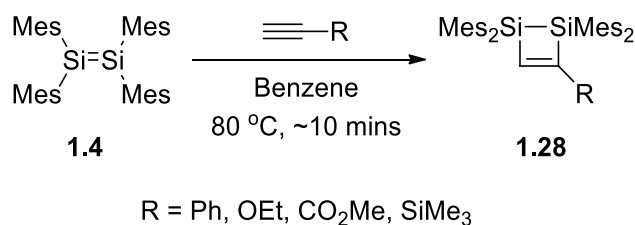
A year later, West reported the addition of acetylenes to two stable disilenes, tetramesityldisilene **1.4** and *trans*-1,2-di-*t*-butyl-1,2-dimesityldisilene **1.25**.³¹ The latter reacted with phenylacetylene and ethoxyacetylene, to afford both the *cis* and *trans* disilacyclobutenes **1.26** and **1.27** in approximately equal amounts (Scheme 1.16). West proposed that the addition of acetylene to **1.26** also proceeds through a biradical

intermediate. However, unlike Sakurai's study, the reaction did not proceed stereoselectively. It was concluded that the lifetime of the putative biradical intermediate is longer than that of the biradical intermediate proposed by Sakurai, allowing more time to scramble the stereochemistry of the substituents before ring closure.



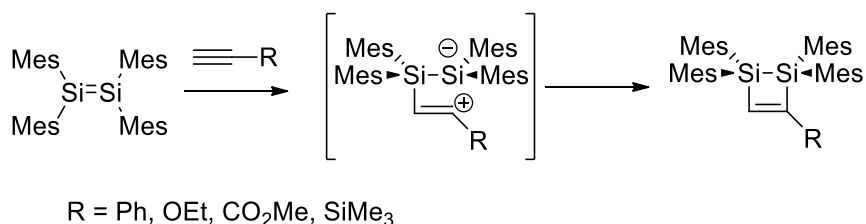
Scheme 1.16: Reaction of disilene **1.25** with phenylacetylene and ethoxyacetylene.

In the case of disilene **1.4**, reaction with phenylacetylene, ethoxyacetylene, carbomethoxyacetylene and trimethylsilylacetylene afforded the corresponding disilacyclobutenes **1.28** (Scheme 1.17). 1-hexyne, 1-phenyl-2-trimethylsilylacetylene, propyne, acetylene, diphenylacetylene, and 3-hexyne-2,5-dione did not react with the disilene.



Scheme 1.17: Reaction of disilene **1.4** with various alkynes.

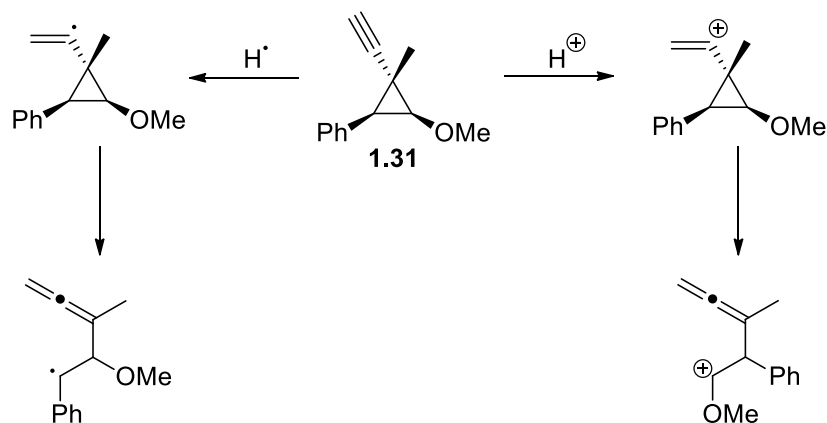
The reactivity pattern observed led West to the conclusion that a zwitterionic intermediate may be involved in the reaction of **1.4** with polarized alkynes. West proposed that the alkyne reacts as the nucleophile in the reaction (Scheme 1.18). Notably West stated: “Further studies will be needed to elucidate the mechanism of alkyne cycloaddition to stable disilenes.”³¹



Scheme 1.18: Stepwise addition of various polar acetylenes forming a zwitterionic intermediate.

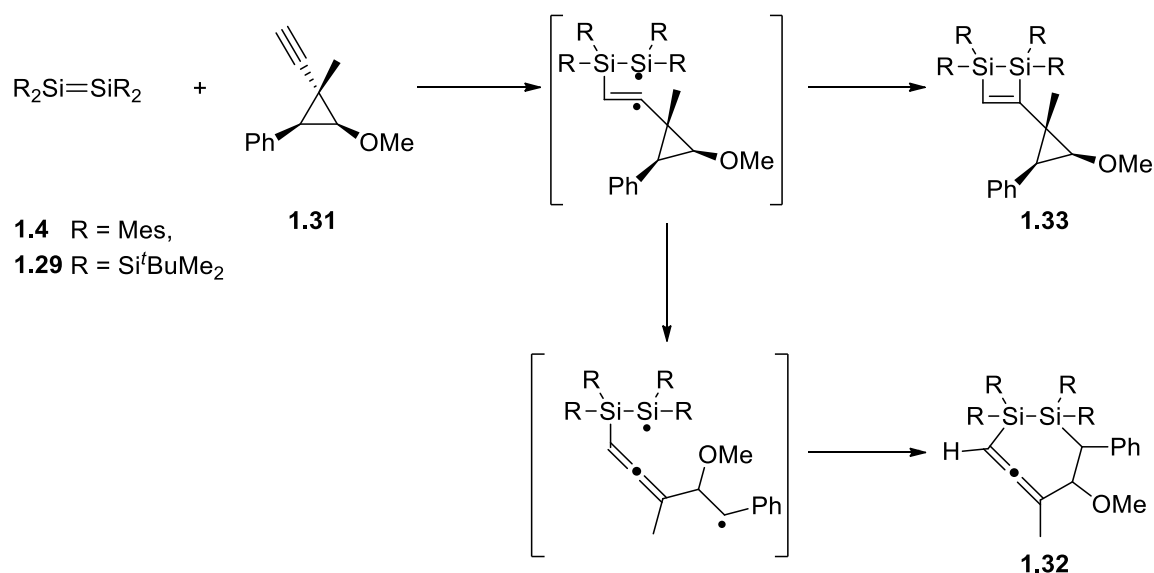
Almost a decade later, the mechanism of the addition of alkynes to disilenes was examined utilizing a mechanistic probe. The rapid ring opening reaction of cyclopropyl carbonyl radicals has effectively been utilized to determine if a radical is present during the course of a reaction.³² To be an effective probe, the rate constant of the ring opening

rearrangement must be greater than the rate constant for any other competitive process. The incorporation of a phenyl substituent on the cyclopropyl ring increases the rate constant for rearrangement of cyclopropyl carbinyl radicals by orders of magnitude.³³ Newcomb reported a cyclopropyl probe with an alkoxy substituent present on the cyclopropyl ring, in addition to the phenyl substituent. This cyclopropyl ring opens regioselectively depending on whether a cation or a radical is located on the carbinyl carbon.³⁴ If a radical is generated adjacent to the cyclopropyl ring, the ring opens regioselectively towards the phenyl group. However, if a cation is generated adjacent to the cyclopropyl ring, the ring opens towards the alkoxy group. By identifying the location of the phenyl and alkoxy substituents in the final product, the nature of the intermediate can be determined. Based on Newcomb's research,^{33,34} cyclopropyl alkyne **1.31** was designed and synthesized.³⁵ The cyclopropyl ring of **1.31** regioselectively opens in the presence of a vinylic cation or radical with rate constants in the range of $10^{10} - 10^{12} \text{ s}^{-1}$ (Scheme 1.19).³⁶



Scheme 1.19: Reactivity of **1.31**, under radical and cationic conditions.

Cyclopropyl alkyne **1.31** was used to study the mechanism of the addition of alkynes to disilenes **1.4**³⁷ and **1.29**.³⁸ In both cases, a disilacyclohepta-3,4-diene was formed as well as a disilacyclobutene (Scheme 1.20). The regiochemistry of the phenyl and methoxy substituents in **1.32** confirms that a biradical intermediate is formed along the reaction pathway. The formation of **1.33** illustrates that ring closure of the biradical intermediate, to give disilacyclobutenes **1.33**, competes with the ring opening rearrangement of the cyclopropyl ring.



Scheme 1.20: Formation of disilacyclobutene **1.33** and disilacyclohepta-3,4-diene **1.32** from the reaction of disilenes with alkyne **1.31**.

Cyclopropyl alkyne **1.31** has been used to study the mechanism of the addition of alkynes to a variety of (di)tetrelenes. The experimental studies have been complemented by computational studies of the mechanism of the addition of alkynes to naturally

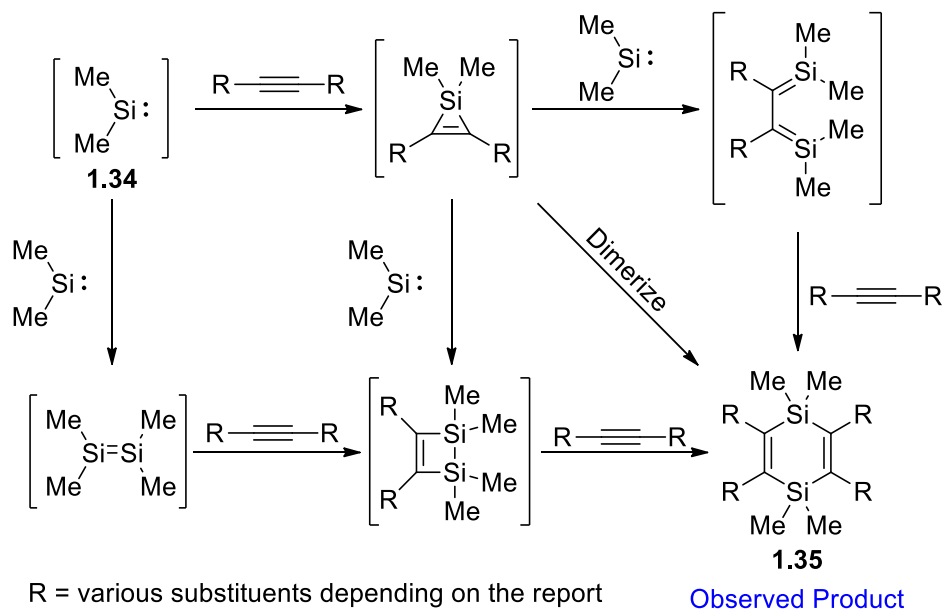
polarized silenes and germenenes.³⁹ A summary of the experimental mechanistic studies is presented in Table 1.1.

Table 1.1: Summary of mechanistic pathways of the reactions between (di)tetrelenes with alkyne **1.31**.

(Di)tetrelene	Chemical Structure	Intermediate
Disilene (aryl ³⁷ or silyl ³⁸ substituents)	$ \begin{array}{ccc} \text{Mes} & & \text{Me}^t\text{Bu}_2\text{Si} \\ & \diagdown & / \\ & \text{Si}=\text{Si} & \\ & / & \diagdown \\ \text{Mes} & & \text{Si}^t\text{Bu}_2\text{Me} \\ & \diagup & \backslash \\ & & \text{Me}^t\text{Bu}_2\text{Si} \end{array} $	Biradical
Digermene ⁴⁰	$ \begin{array}{ccc} \text{Mes} & & \text{Mes} \\ & \diagdown & / \\ & \text{Ge}=\text{Ge} & \\ & / & \diagdown \\ \text{Mes} & & \text{Mes} \end{array} $	Biradical
Silene ⁴¹	$ \begin{array}{ccc} \text{Me}_3\text{Si} & & \text{OSiMe}_3 \\ & \diagdown & / \\ & \text{Si} & \\ & / & \diagdown \\ \text{Me}_3\text{Si} & & ^t\text{Bu} \end{array} $	Biradical

Understanding the mechanism of the cycloaddition of alkynes to silylenes is equally as critical for the development of this area of chemistry. Silylenes exist in the singlet ground state and have a lone pair of electrons and an empty p-orbital. As a consequence, they can behave as either a nucleophile or an electrophile. Early mechanistic studies were undertaken on the reactivity of transient silylenes. The reaction of transient silylene **1.34**, generated from either the reaction of dimethylchlorosilane and sodium or thermal cleavage of the silicon-silicon bonds in polydimethylsilane, with alkynes has been extensively studied. Multiple pathways for the formation of disilahexadiene **1.35** have been proposed on the basis of kinetic and product studies

which include pathways involving disilene, silacyclopentene, and disilacyclobutene intermediates (Scheme 1.21).⁴²



Scheme 1.21: Potential pathways for the formation of 1,4-disilahexadiene **1.35**.

While the multiple ways to generate the transient silylene **1.34** and the varying substituents on the alkynes makes it difficult to compare all the reports, the overarching conclusion is that the transient silylene **1.34** can dimerize and then react with the alkyne or add the alkyne to form a silacyclopentene which then undergoes further reactions.

The cycloaddition of silylenes with alkynes has been studied computationally using density functional theory methods. Two different reaction pathways were examined: the least motion pathway where the silylene acts as a nucleophile, and the non-least motion pathway where the silylene acts as an electrophile (Figure 1.1).⁴³

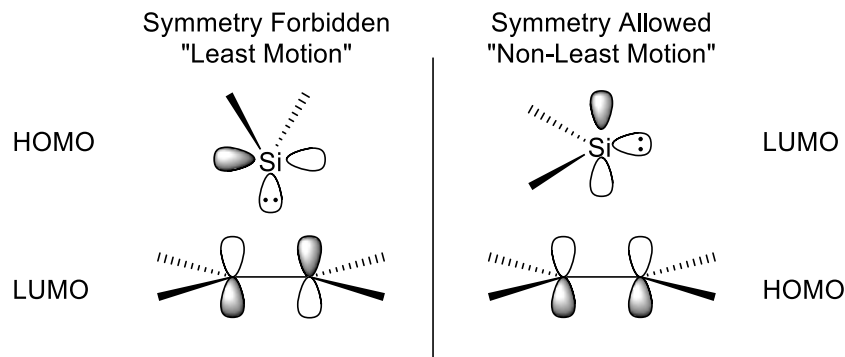
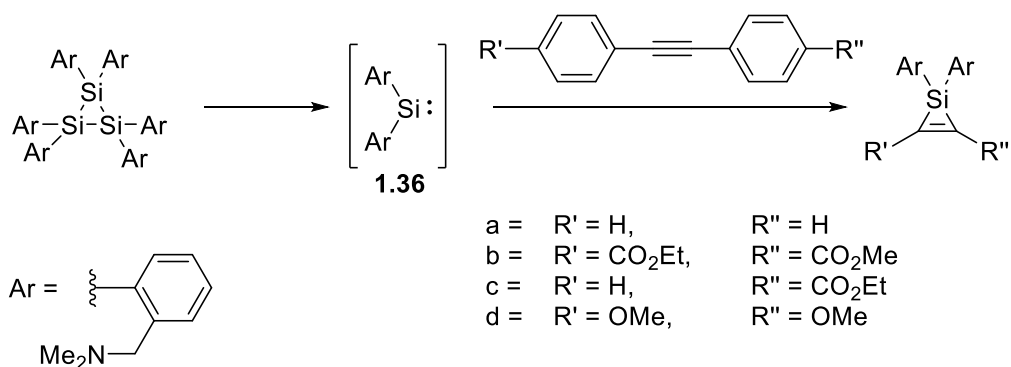


Figure 1.1: The two different orientations of orbital overlap between silylene and the π -orbitals of an alkyne

In the “least motion” pathway, the interaction between the lone pair of the silylene and the LUMO of the alkyne is forbidden by symmetry, whereas, the “non-least motion” pathway is symmetry-allowed where the filled π -orbitals of the alkyne (HOMO) can overlap with the empty p -orbital of the silylene (LUMO). The results indicated that the cycloaddition of alkynes to silylenes proceeds through the symmetry allowed “non-least motion” pathway where the silylene acts as an electrophile.

As is well-recognized, the nature of the substituents can greatly influence the reaction mechanism. The reactivity of the bis(aryl)silylene **1.36** with a variety of acetylenes was examined (Scheme 1.22).⁴⁴



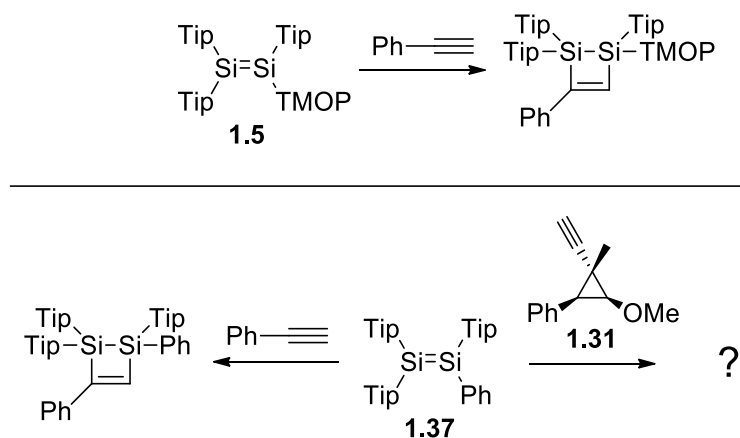
Scheme 1.22: Generation of transient silylene **1.36** and subsequent addition of various acetylenes.

A Hammett study provided insight into the philicity of silylene **1.36**. The positive reaction constant ($\rho = +0.85 \pm 0.21$) was comparable to that of the reaction of cycloheptatrienyliidene, a nucleophilic carbene, and styrene suggesting that the silylene acts as a nucleophile in contrast to previous studies where the silylene acts as the electrophile. The nucleophilic character of silylene **1.36** is attributed to coordination of the *ortho*-NMe₂ groups with the silicon centre reducing the electrophilicity of the silylene.

1.4 Project Overview

Scheschkewitz examined the addition of phenylacetylene to two disilenes, **1.5** and **1.37** (Scheme 1.23). In each case, disilacyclobutenes were obtained regioselectively. To account for the regioselectivity of the reaction, Scheschkewitz proposed the formation of

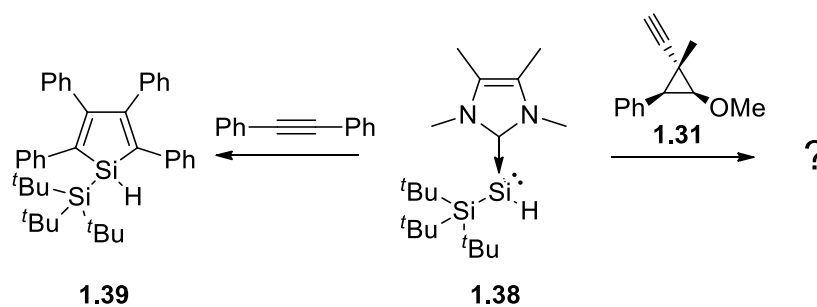
a zwitterionic intermediate during the course of the reaction because of the expected polarization of the unsymmetrically-substituted silicon-silicon double bond. The Baines group has previously reported that tetramesityldisilene **1.4**, a tetraryl-substituted disilene, in the reaction with alkynes proceeds through a reaction pathway involving a biradical intermediate. Given that **1.5** and **1.37** are also tetraaryldisilenes, it is reasonable that the mechanism of the reaction be the same. Chapter 2 describes the addition of cyclopropylalkyne **1.31** to disilene **1.37** in an effort to determine the nature of the reaction intermediate.



Scheme 1.23: Addition of phenylacetylene to **1.5** and **1.37**. Chapter 2 examines the addition of **1.31** to **1.37**.

The coordination of Lewis bases is an effective method for the stabilization of silylenes. While simple alkyl- and aryl-substituted silylenes react with alkynes to form a variety of products derived from silacyclopropenes, base-stabilized silylenes typically yield a silole upon reaction with an alkyne. For example, Inoue synthesized the NHC-stabilized silylene **1.38** and observed the formation of **1.39** upon the addition of

diphenylacetylene (Scheme 1.24).⁴⁵ On the basis of a computational study, Inoue proposed that the reaction proceeds through a zwitterionic intermediate where the silylene acts as a nucleophile. In Chapter 3, the reaction of silylene **1.38** with alkyne **1.31** was investigated in an effort to determine the nature of the reaction intermediate.



Scheme 1.24: Addition of diphenylacetylene to silylene **1.38**. Chapter 3 examines the addition of **1.31** to **1.38**.

1.5 References

1. a) Okazaki, R.; West, R.; *Adv. Organomet. Chem.*, **1996**, *39*, 231; b) Weidenbruch, M.; *Coord. Chem. Rev.*, **1994**, *130*, 275; c) Raabe, G.; Michl, J.; *Chem. Rev.*, **1985**, *85*, 419; d) Ottosson, H.; Steel, P. G.; *Chem. Eur. J.*, **2006**, *12*, 1576.
2. a) Masamune, S.; Murakami, S.; Tobita, H.; *Organometallics* **1983**, *2*, 1464; b) Schäfer, A.; Weidenbruch, M.; *J. Organomet. Chem.* **1985**, *282*, 305.
3. Roark, D. N.; Peddle, G. J. D.; *J. Am. Chem. Soc.*, **1972**, *94*, 5837.
4. Sakurai, H.; Kobayashi, T.; Nakadaira, Y.; *J. Org. Chem.*, **1978**, *162*, C43.
5. West, R.; Fink, M. J.; Michl, J.; *Science*, **1981**, *214*, 1343.
6. 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.
7. a) De Young, D. J.; Fink, M. J.; West, R.; *Main Group Met. Chem.*, **1987**, *10*, 19; b) Fink, M. J.; De Young, D. J.; West, R.; Michl, J.; *J. Am. Chem. Soc.*, **1983**, *105*, 1070.
8. Meltzer, A.; Majumdar, M.; White, A. J. P.; Huch, V.; Scheschkewitz, D.; *Organometallics*, **2013**, *32*, 6844.
9. Iwamoto, T.; Sakurai, H.; Kira, M.; *Bull. Chem. Soc. Jpn.*, **1998**, *71*, 2741.
10. Atwell, W. H.; *Angew. Chem. Int. Ed.*, **1969**, *8*, 469.

11. Suzuki, H.; Tokitoh, N.; Okazaki, R.; *Bull. Chem. Soc. Jpn.*, **1995**, *68*, 2471.
12. Ishikami, M.; Sugisawa, H.; Kumada, M.; *J. Organomet. Chem.*, **1977**, *142*, C45.
13. Ishikawa, M.; Sugisawa, H.; Kumada, M.; Kawakami, H.; Yamabe, T.; *Organometallics*, **1983**, *2*, 974.
14. Lips, F.; Mansikkamaki, A.; Fettinger, J. C.; Tuononen, H. M.; Power, P. P.; *Organometallics*, **2014**, *33*, 6253.
15. Lebedev, Y. N.; Das, U.; Chernov, O.; Schnakenburg, G.; Filippou, A. C.; *Chem. Eur. J.*, **2014**, *20*, 9280.
16. a) Duke, C. B.; *Chem. Rev.*, **1996**, *96*, 1237; b) Buriak, J. M.; *Chem. Rev.*, **2002**, *102*, 1271; c) Wolkow, R. A.; *Annu. Rev. Phys. Chem.*, **1999**, *50*, 413.
17. a) Yates, J. T., Jr. *Science*, **1998**, *279*, 335; b) Hamers R. J.; Coulter, S. K.; Ellison, M. D.; Hovis, J. S.; Padowitz, D. F.; Schwartz, M. P.; *Acc. Chem. Res.*, **2000**, *33*, 617; c) Bent, S. F.; *Surf. Sci.*, **2002**, *500*, 879.
18. Liu, Q.; Hoffmann, R.; *J. Am. Chem. Soc.*, **1995**, *117*, 4082.
19. Lu, X.; Zhu, M.; Wang, X.; Zhang, Q.; *J. Phys. Chem. B*, **2004**, *108*, 4478.
20. Majumdar, M.; Bejan, I.; Huch, V.; White, A. J. P.; Whittell, G. R.; Schäfer, A.; Manners, I.; Scheschkewitz, D.; *Chem. Eur. J.*, **2014**, *20*, 9225.
21. Ishikawa, M.; *Asian J. Org. Chem.*, **2015**, *4*, 1192.

22. Clark, T. B.; Woerpel, K. A.; *Org. Lett.*, **2006**, *8*, 4109.
23. Anderson, L. L.; Woerpel, K. A.; *Org. Lett.*, **2009**, *11*, 425.
24. a) Johannsen, M.; Jørgensen, K. A.; *Chem. Rev.*, **1998**, *98*, 1698. b) Trost, B. M.; Crawley, M. L.; *Chem. Rev.*, **2003**, *103*, 2921.
25. Palmer, S. P.; Woerpel, K. A.; *Organometallics*, **1997**, *16*, 4824.
26. a) Zhao, Z.; He, B.; Tang, B. Z.; *Chem. Sci.*, **2015**, *6*, 5347; b) Chen, B.; Jiang, Y.; Chen, L.; Nie, H.; He, B.; Lu, P.; Sung, H. H. Y.; Williams, I. D.; Kwok, H. S.; Qin, A.; Zhao, Z.; Tang, B. Z.; *Chem. Eur. J.*, **2014**, *20*, 1931.
27. a) Emanuelsson, R.; Denisova, A. V.; Baumgartner, J.; Ottosson, H.; *Organometallics*, **2014**, *33*, 2997; b) Tibbelin, J.; Wallner, A.; Emanuelsson, R.; Heijkenskjöld, F.; Rosenberg, M.; Yamazaki, K.; Nauroozi, D.; Karlsson, L.; Feifel, R.; Pettersson, R.; Baumgartner, J.; Ott, S.; Ottosson, H.; *Chem. Sci.*, **2014**, *5*, 360.
28. a) Hoffmann, R.; Woodward, R. B.; *Acc. Chem. Res.*, **1968**, *1*, 17; b) Woodward, R. B.; Hoffmann, R.; *Angew. Chem. Int. Ed.*, **1969**, *8*, 781.
29. Nakadaira, Y.; Sato, R.; Sakurai, H.; *Chem. Lett.*, **1985**, *14*, 643.
30. Sakurai, H.; Kobayashi, T.; Nakadaira, Y.; *J. Am. Chem. Soc.*, **1979**, *101*, 487.
31. De Young, D. J.; West, R.; *Chem. Lett.*, **1986**, *15*, 883.

32. a) Cooksy, A. L.; King, H. K.; Richardson, W. H.; *J. Org. Chem.*, **2003**, *68*, 9441; b) Tanko, J. M.; Blackert, J. F.; *J. Chem. Soc., Perkin Trans. 2*, **1996**, 1775.
33. Newcomb M.; *Tetrahedron*, **1993**, *49*, 1151.
34. Le Tadic-Biadatti, M.-H.; Newcomb, M. *J. Chem. Soc., Perkin Trans. 2*, **1996**, 1467.
35. Gottschling, S. E.; Grant, T. N.; Milnes, K. K.; Jennings, M. C.; Baines, K. M.; *J. Org. Chem.*, **2005**, *70*, 2686.
36. Milnes, K. K.; Gottschling, S. E.; Baines, K. M.; *Org. Biomol. Chem.*, **2004**, *2*, 3530.
37. Gottschling, S. E.; Milnes, K. K.; Jennings, M. C.; Baines, K. M.; *Organometallics*, **2005**, *24*, 3811.
38. Gottschling, S. E.; Jennings, M. C.; Baines, K. M.; *Can. J. Chem.*, **2005**, *83*, 1568.
39. Pavelka, L. C.; Hanson, M. A.; Staroverov, V. N.; Baines, K. M.; *Can. J. Chem.*, **2015**, *93*, 134.
40. Hurni, K. L.; Baines, K. M.; *Chem. Commun.*, **2011**, *47*, 8382.
41. a) Milnes, K. K.; Jennings, M. C.; Baines, K. M.; *J. Am. Chem. Soc.*, **2006**, *128*, 2491.; b) Milnes, K. K.; Baines, K. M.; *Can. J. Chem.*, **2009**, *87*, 307.
42. Atwell, W. H.; *Organometallics*, **2009**, *28*, 3573.

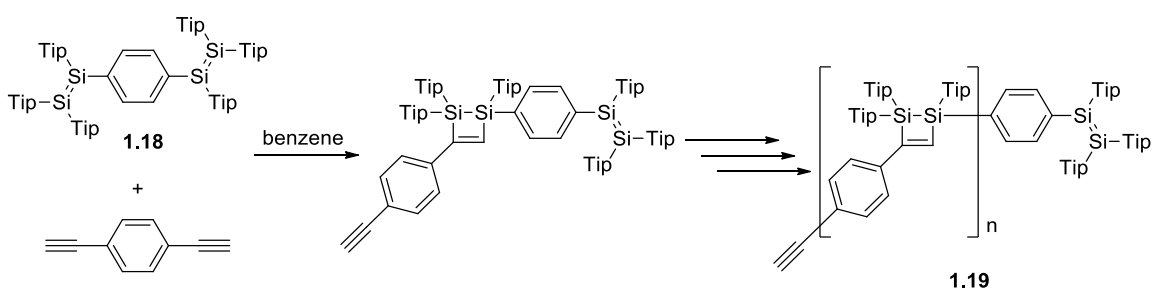
43. a) Koch, R.; Bruhn, T.; Weidenbruch, M.; *Organometallics*, **2004**, *23*, 1570; b)
Tanaka, H.; Kondo, Y.; Shioita, Y.; Naka, A.; Ishikawa, M.; Yoshizawa, K.;
Organometallics, **2011**, *30*, 3160.
44. Belzner, J.; Dehnert, U.; Ihmels, H.; *Tetrahedron*, **2001**, *57*, 511.
45. Eisenhut, C.; Szilvsi, T.; Breit, N. C.; Inoue, S.; *Chem. Eur. J.*, **2015**, *21*, 1949.

Chapter 2

2 Investigation into the Mechanism of the Addition of a Cyclopropyl Alkyne to an Asymmetrical Disilene

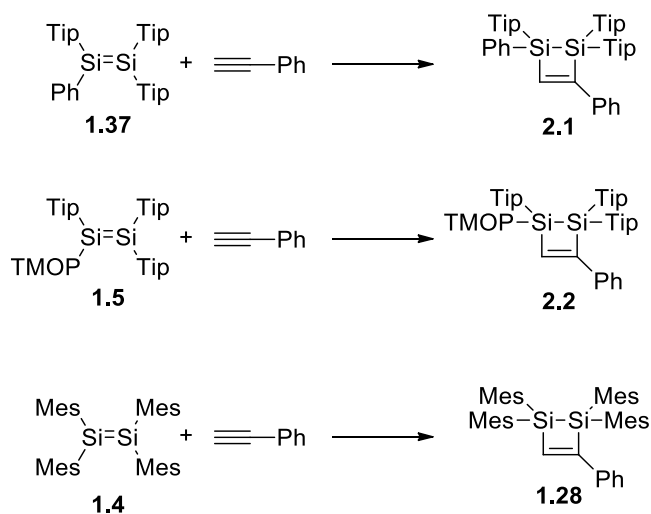
2.1 Introduction

The chemistry of disilenes has been studied extensively over the past 40 years. The cycloaddition reactions with disilenes have remained a focus of research due to the ability to form complex ring structures cleanly and rapidly.¹ The cycloaddition of alkynes to disilenes has been shown to generate a disilacyclobutene. Due to the favourable characteristics of the reaction, it has been used in a variety of applications. For example, an organosilicon polymer was synthesized where the cycloaddition between an phenylene-bridged bis(disilene) and a phenylene-bridged dialkyne was the key oligomerization step (Scheme 2.1).³



Scheme 2.1: Polymerization of the linker bridged tetrasiladiene **1.18** with 1,4-diethynyl benzene.

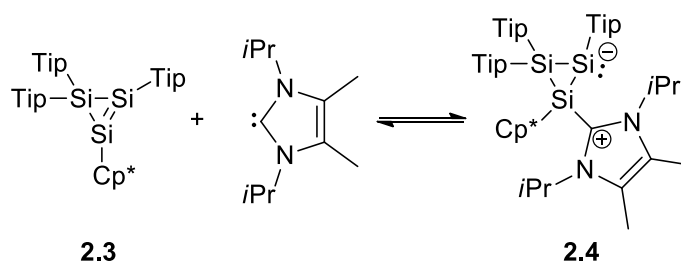
Mechanistic studies of the addition of alkynes to disilenes have focused on the chemistry of disilenes with four identical substituents, while minimal work has been done on polarized silicon-silicon double bonds from asymmetrically-substituted disilenes. In 2007, Scheschkewitz reported the synthesis of disilenes **1.5** and **1.37**, which feature three 2,4,6-triisopropylphenyl substituents and one different aryl substituent.² The synthesis of asymmetrically-substituted disilenes allowed an examination of the regiochemistry of the addition reactions of a variety of reagents. Addition of a terminal alkyne to disilene **1.5** and **1.37** resulted in the regioselective formation of disilacyclobutene **2.1** and **2.2**.^{3,4} When compared to the disilene **1.4**, the same reactivity is observed (Scheme 2.2).⁵



Scheme 2.2: Cycloaddition of phenylacetylene to asymmetrically-substituted disilenes **1.37** and **1.5**, and the symmetrically substituted **1.4**.

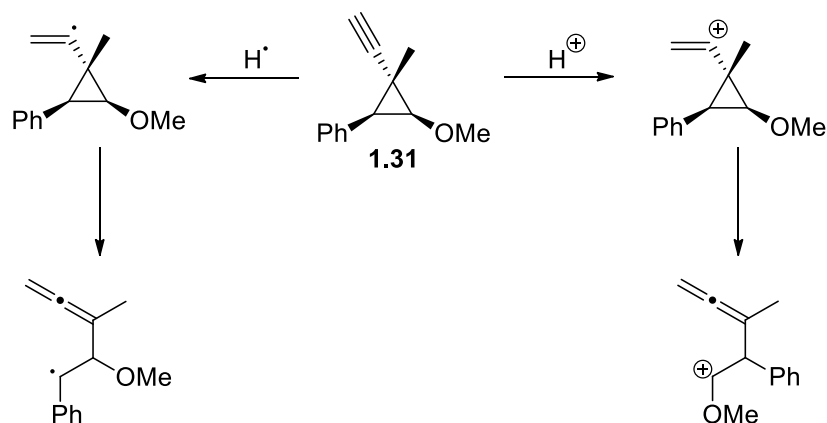
The regioselectivity of the cycloaddition reaction suggests the selective formation of an intermediate. Although Scheschkewitz recognized that symmetrically-substituted disilenes have been shown to proceed via the formation of a biradical intermediate, he

proposed that disilene **1.37**, due to the polarization of the silicon-silicon double bond, would favour the formation of a zwitterionic intermediate.³ The reversible coordination of an N-heterocyclic carbene to cyclotrisilene **2.3** was provided as evidence in support of a zwitterionic intermediate in the addition of alkynes to **1.37** (Scheme 2.3).⁶ Adduct **2.4** was formed regioselectively with the NHC adding to the less hindered Cp*-substituted silicon atom of the disilene.



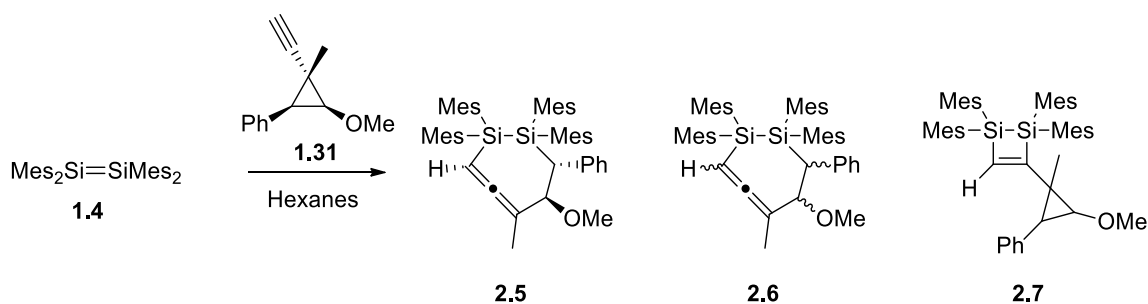
Scheme 2.3: Reaction of a donor NHC with the asymmetric disilene moiety in **2.3**.

The mechanism of the addition of alkynes to a disilene with four identical aryl substituents, **1.4**, was examined utilizing the cyclopropyl alkynyl probe **1.31**.⁷ Probe **1.31** is able to distinguish between the formation of a cyclopropyl vinyl radical or cation by undergoing regioselective ring opening towards the phenyl or methoxy group, respectively, on the cyclopropyl ring (Scheme 2.4).⁸



Scheme 2.4: Regioselective ring opening of cyclopropyl alkyne probe **1.31** upon addition of a radical or a cation.

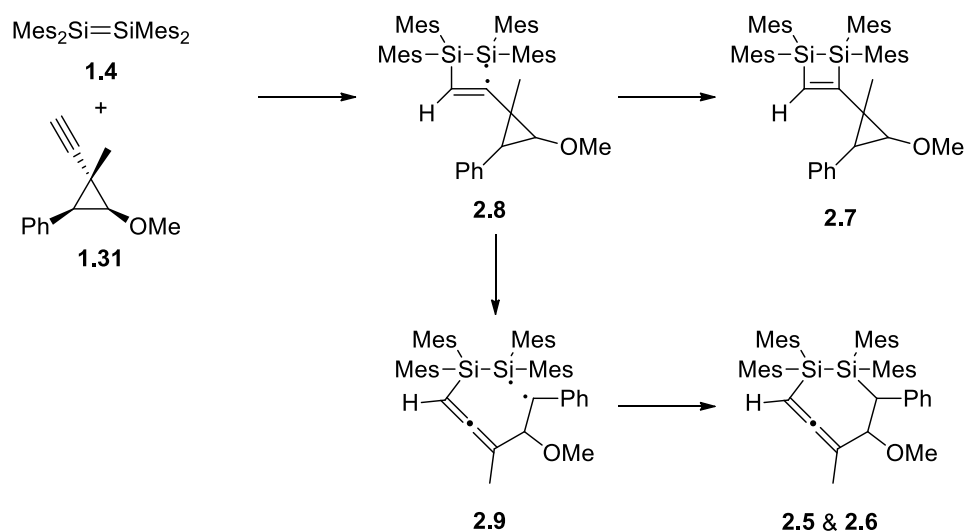
Thus, by examination of the regiochemistry of the products, one can determine the nature of the intermediate formed along the pathway. The addition of alkyne **1.31** to disilene **1.4** resulted in the formation of three compounds: **2.5** – **2.7** (Scheme 2.5).⁷



Scheme 2.5: Reaction of tetramesityldisilene **1.4** with alkyne **1.31**.

The placement of the phenyl and methoxy substituents in the seven-membered cyclic allenes, **2.5** and **2.6**, leads to the conclusion that a biradical intermediate was formed along the reaction pathway. Similar products were observed with the tetrasilyl-

substituted disilene **1.29** and, as such, was also shown to proceed through a biradical intermediate.⁹ The mechanism for the formation of **2.5** – **2.7** is illustrated in Scheme 2.6. The addition of the alkyne to the disilene results in the formation of the biradical **2.8**. Closure of the biradical gives the disilacyclobutene, **2.7**. Alternatively, the cyclopropyl ring opens to give biradical **2.9** which upon closure gives the allenes **2.5** and **2.6**.



Scheme 2.6: Mechanism for the addition of probe **1.31** to tetramesityldisilene **1.4**.

While mechanistic studies have been done on the addition of alkynes to disilenes with four identical substituents, the mechanism of the addition of an alkyne to a disilene with a dipole moment has yet to be explored. We hypothesize that a tetraaryl disilene will react by the same mechanism with an alkyne despite variations in the nature of the substituents on the aryl group. To provide evidence in support of this hypothesis, the addition of cyclopropyl probe **1.31** to disilene **1.37** has been examined.

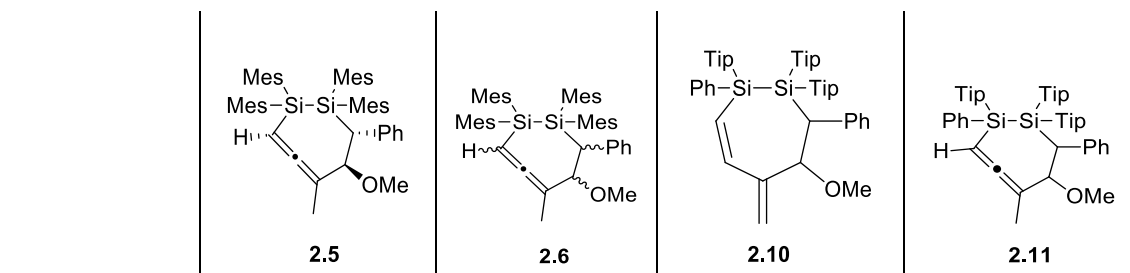
2.2 Results and Discussion

Cyclopropyl alkyne **1.31** was added to an equimolar yellow hexanes solution of disilene **1.37** at room temperature to give a red-orange solution and a light-yellow precipitate. After separation of the light-yellow precipitate by centrifugation, the solvent was removed to yield a red residue. Upon dissolution in DCM and exposure of the solution to air, the red colour of the solution disappeared to yield a clear and colourless solution. The products were separated by preparative thin layer chromatography. Four compounds were isolated, **2.10** -**2.13**; each compound was determined to be a 1:1 adduct between disilene **1.37** and probe **1.31** by mass spectrometry. All compounds were characterized by ^1H , ^{13}C , ^1H - ^1H gCOSY, ^{13}C - ^1H gHSQC, ^{13}C - ^1H gHMBC and ^{29}Si - ^1H gHMBC NMR spectroscopy as well as by ESI-mass spectrometry. Due to the complexity of the spectrum in the 0-2 ppm and 6.5-8.5 ppm regions, the analysis focused on the region between 2.5 – 6 ppm in the ^1H NMR spectra as well as the region between 40 – 110 ppm in the ^{13}C NMR spectra of the products.

2.2.1 Structure Elucidation

The ESI mass spectrum of compound **2.10** revealed a signal at m/z 951.627 which is consistent with the mass expected for a 1:1 adduct between **1.37** and **1.31** (plus a sodium ion). The region from 3.5-5.0 ppm in the ^1H NMR spectrum of **2.10** is shown in Figure 2.1. Interestingly, upon comparison to the crude ^1H NMR spectrum, **2.10** was not found

in the crude mixture and is hypothesized to have formed during chromatography. The spectrum contains two doublets at 4.93 and 4.08 ppm which were assigned to the CH-Ph and CH-OMe hydrogens, respectively, on the basis of the observed correlations to signals at 42.69 ppm and 91.38 ppm in the ^{13}C dimension of the ^{13}C - ^1H gHSQC NMR spectrum of **2.10**, respectively. Since disilene **1.37** is a tetraaryl-substituted disilene, a comparison of the chemical shifts of the products derived from the addition of alkyne **1.31** to tetramesityldisilene **1.4**, **2.5** and **2.6**, and **2.10** is useful.⁷ Diagnostic chemical shifts are highlighted in Table 2.1. The chemical shifts assigned to the CH-OMe and CH-Ph of **2.10** are comparable to the analogous shifts in compounds **2.5** and **2.6** (Table 2.1). Accordingly, a correlation was observed between the two doublets in the ^1H - ^1H gCOSY NMR spectrum of **2.10**. The value of the coupling constant for the doublet was determined to be 10 Hz which is close in magnitude to the corresponding coupling constants of 10 - 12 Hz for the analogous signals in the ^1H NMR spectra of **2.5** and **2.6**. The ^1H chemical shift of CH-Ph at 4.92 ppm is similar to the chemical shifts of analogous hydrogens in the 7-membered ring compounds, **2.5** and **2.6**, and very different compared to the chemical shifts of the analogous hydrogen in compound **2.7**, suggesting that compound **2.10** has a larger ring.

Table 2.1: ^1H NMR and ^{13}C NMR chemical shifts of **2.5**, **2.6**, **2.10**, and **2.11**. **^1H NMR Chemical Shifts**

<u>H</u>CPh	4.54 [J = 12 Hz]	4.49 [J = 10 Hz]	4.93 [J = 10 Hz]	4.01
<u>H</u>COCH₃	4.60 [J = 12 Hz]	4.17 [J = 10 Hz]	4.08 [J = 10 Hz]	3.70
<u>CH</u>₃	1.80	1.32	-	1.33
O<u>CH</u>₃	3.00	2.93	2.20	3.02
C=C=<u>CH</u>	5.50	6.22	-	6.71

 ^{13}C NMR Chemical Shifts

<u>H</u>CPh	52.42	44.1	42.69	54.08
<u>H</u>COCH₃	77.07	84.4	91.38	92.23
O<u>CH</u>₃	56.62	51.9	57.10	56.80
C=<u>C</u>=C	213.14	210.2	-	218.32

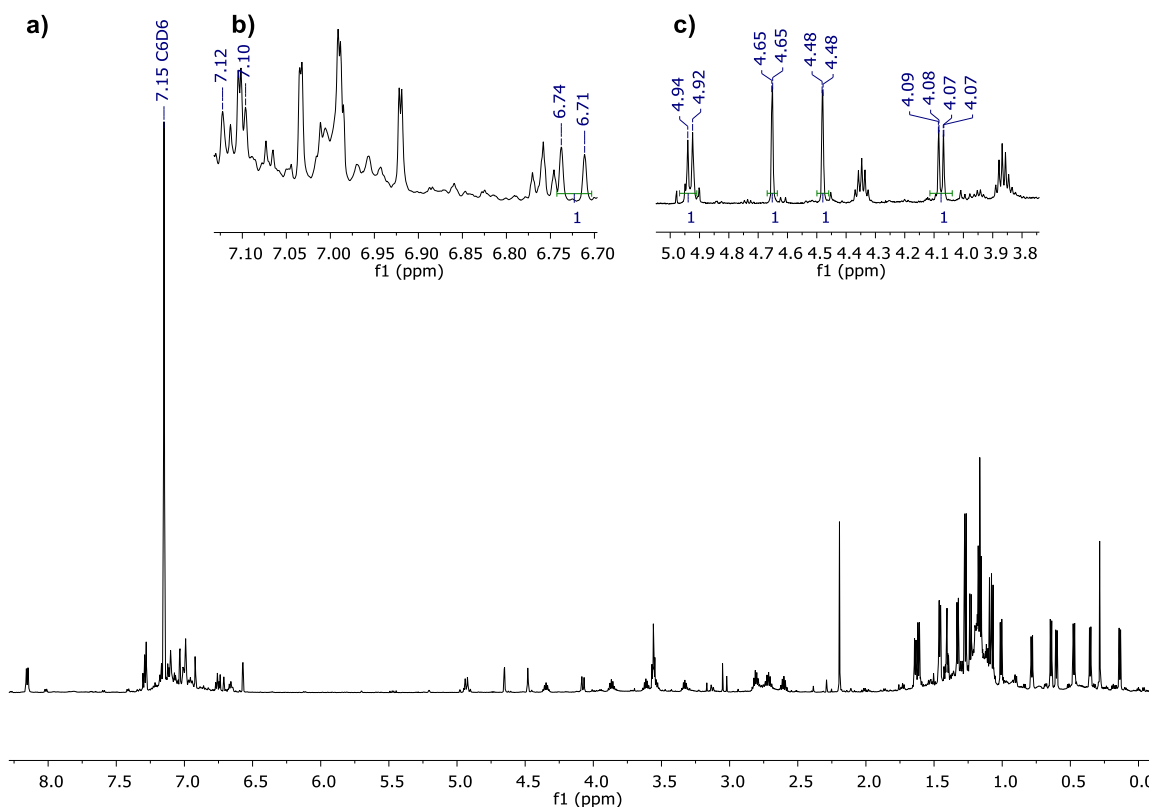


Figure 2.1: a) ^1H NMR spectrum (600 MHz, C_6D_6) of **2.10**; b) Expansion from 6.70 – 7.12 ppm; c) Expansion from 3.8-5.0 ppm.

Correlations in the ^{13}C - ^1H gHMBC and ^{13}C - ^1H gHSQC NMR spectra of **2.10** were utilized to construct the core fragment (Figure 2.2). While the doublet assigned to the $\underline{\text{CH}}$ -Ph moiety correlated to signals in the aromatic region of the ^{13}C dimension of the ^{13}C - ^1H HMBC spectrum of **2.10**, the signal assigned to the $\underline{\text{C}}\text{H}$ -OMe group only correlated to two singlets in the ^1H dimension in the ^{13}C - ^1H gHMBC NMR spectrum of **2.10** at 4.65 and 4.48 ppm. The two singlets both correlated to the same ^{13}C at 123.76 ppm in the ^{13}C dimension of the ^{13}C - ^1H HSQC NMR spectrum of **2.10**.¹⁰ Together, the assignments lead to the fragment shown in Chart 2.1a.

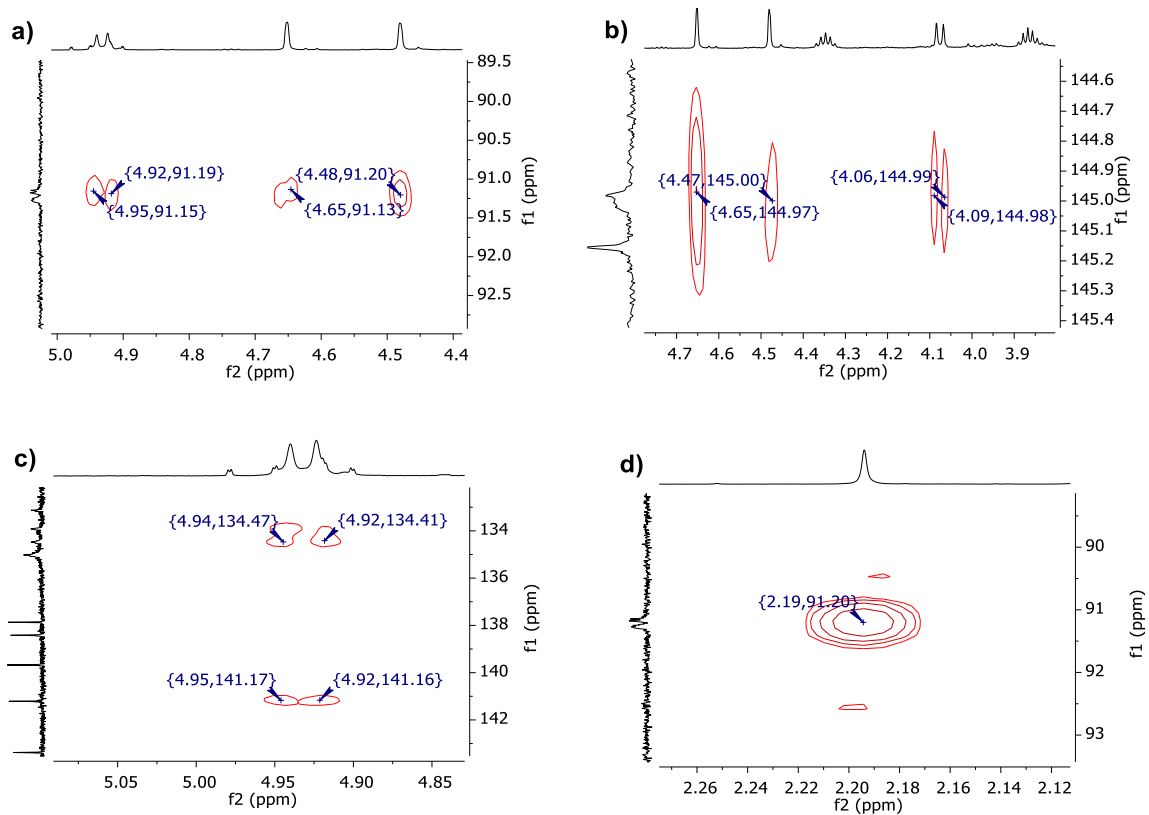


Figure 2.2: Expansion of the ^{13}C - ^1H gHMBC NMR spectrum of **2.10** (600 MHz, C_6D_6) with ^1H ranges of: a) 4.40-5.00 ppm; b) 3.85-4.75 ppm; c) 4.85-5.05 ppm; d) 2.12-2.26 ppm.

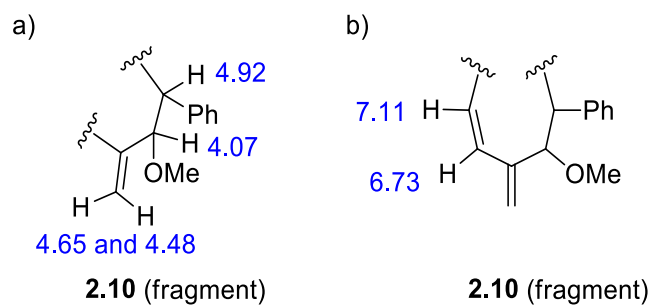


Chart 2.1: Fragments of **2.10** highlighting key ^1H signals in blue.

A correlation between the signals at 4.65 ppm and 4.48 ppm in the ^1H dimension and a signal at 145.16 ppm in the ^{13}C dimension of the ^{13}C - ^1H gHMBC NMR spectrum of **2.10** was observed and assigned to an alkenyl carbon. The signal assigned to this carbon correlates to a doublet at 6.73 ppm in the ^1H dimension of the ^{13}C - ^1H gHSQC NMR spectrum. Furthermore, the doublet at 6.73 ppm correlates to a signal at 133.29 ppm in the ^{13}C dimension of the ^{13}C - ^1H gHMBC NMR spectrum, and this signal correlates to a doublet in the ^1H dimension at 7.11 ppm in the ^{13}C - ^1H gHSQC NMR spectrum. While the doublets at 6.73 and 7.11 ppm in the ^1H NMR spectrum of **2.10** are masked by other signals in benzene- d_6 , using acetone- d_6 as the solvent, allowed for the determination of the coupling constant of the doublet (16 Hz). Together, the assignments give us the fragment shown in Chart 2.1b.

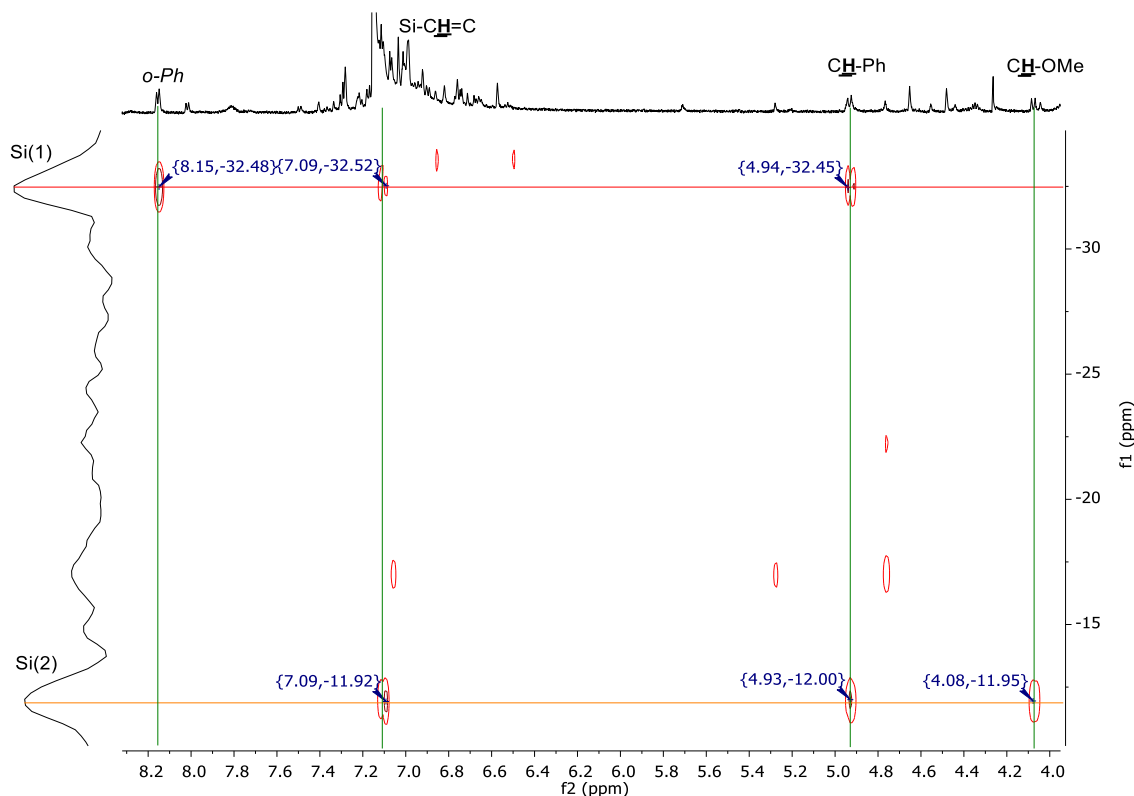


Figure 2.3: Expansion of the ^{29}Si - ^1H gHMBC NMR spectrum of **2.10** (600 MHz, C_6D_6). The signals at -32 and -12 ppm in the ^{29}Si dimension are noted as Si(1) and Si(2) respectively.

Notably, the signals at -12 ppm and -32 ppm in the ^{29}Si dimension of the ^{29}Si - ^1H gHMBC NMR spectrum of **2.10**, both correlated to the same signal at 4.93 ppm in the ^1H dimension which was assigned to the CH-Ph moiety. However, only the signal at -12 ppm in the ^{29}Si dimension correlated to the signal at 4.07 ppm in the ^1H dimension which was assigned to the CH-OMe moiety. These correlations, plus the chemical shift of CH-Ph , provides convincing evidence that the CH-Ph group is bound directly to the Si atom with a chemical shift of -12 ppm. Similarly, both ^{29}Si signals correlated to the signal at 7.11 ppm in the ^1H dimension, which was assigned to an alkenyl hydrogen, while only

the signal at -32 ppm correlated to the signal at 6.73 ppm in the ^1H dimension which was also assigned to an alkenyl hydrogen. This leads to the conclusion that the alkenyl moiety is bound directly to the Si atom with a chemical shift at -32 ppm. Furthermore, the signal in the ^{29}Si dimension at -32 ppm correlates to a doublet at 8.15 ppm in the ^1H dimension which was assigned to an *o*-Ph-H on the basis of its splitting pattern, chemical shift, and correlations to other signals in the aromatic region of the ^{13}C dimension of the ^{13}C - ^1H gHMBC spectrum of **2.10**. Thus, the phenyl group is attached to the Si with a chemical shift of -32 ppm (Chart 2.2).

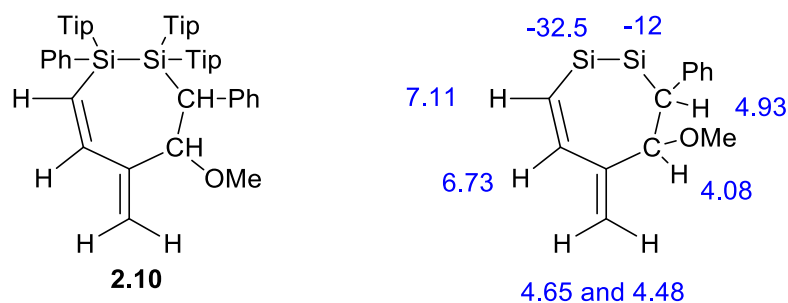


Chart 2.2: Elucidated structure for **2.10** highlighting key ^1H signals in blue.

Recrystallization from a minimal amount of acetone yielded single crystals of **2.10** giving the molecular structure shown in Figure 2.4 confirming the structure elucidated by NMR spectroscopy. Both enantiomers of **2.10** were observed in the asymmetric unit.

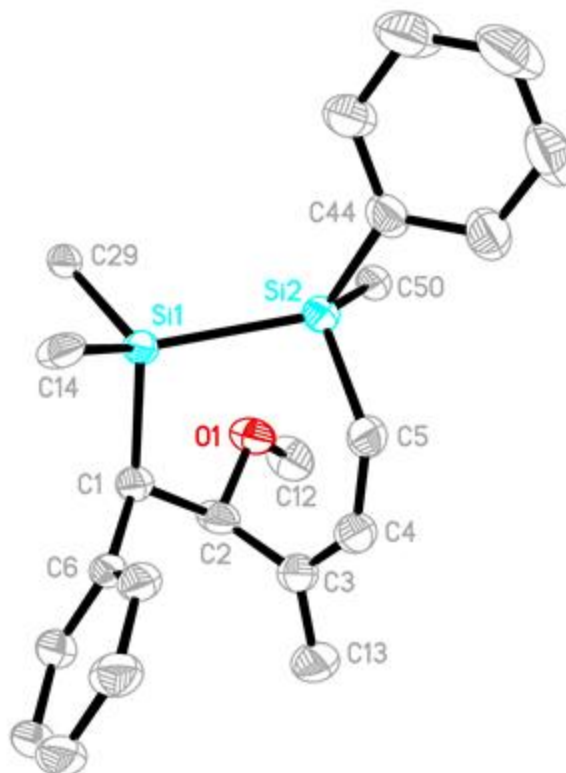


Figure 2.4: Ellipsoid plot of **2.10** showing naming and numbering scheme. Ellipsoids are at the 50% probability level, all ligand-based hydrogen atoms and Tip groups (except the *i*-carbon) were omitted for clarity. Selected bond lengths (Å) and angles (°): Si1-Si2 = 2.4795(10), C4-C5 = 1.345(4), C3-C13 = 1.340(4), Si1-Si2-C5 = 97.21(8), Si2-C5-C4 = 136.4(2), C5-C4-C3 = 129.9(3), C4-C3-C2 = 120.8(2), C3-C2-C1 = 115.1(2), C2-C1-Si1 = 117.05(16), C1-Si1-Si2 = 102.07(7).

The molecular structure confirms the regiochemistry of the phenyl and methoxy substituents in **2.10**. The phenyl substituent on Si2 and the phenyl substituent on C1 are *cis* to each other, whereas the phenyl and methoxy substituents on C1 and C2, respectively, are *trans* reducing steric interactions. The C4-C5 and C3-C13, bond lengths at 1.345(4) Å and 1.340(4) Å, respectively, are consistent with C=C double bonds.

The ^1H NMR spectrum, of **2.11** is illustrated in Figure 2.5. The ESI mass spectrum of **2.11** revealed a signal at m/z 951.627 indicative of a 1:1 adduct between alkyne **1.31** and disilene **1.37**. A similar strategy to that used in the identification of **2.10** was applied to elucidate the structure of **2.11**.

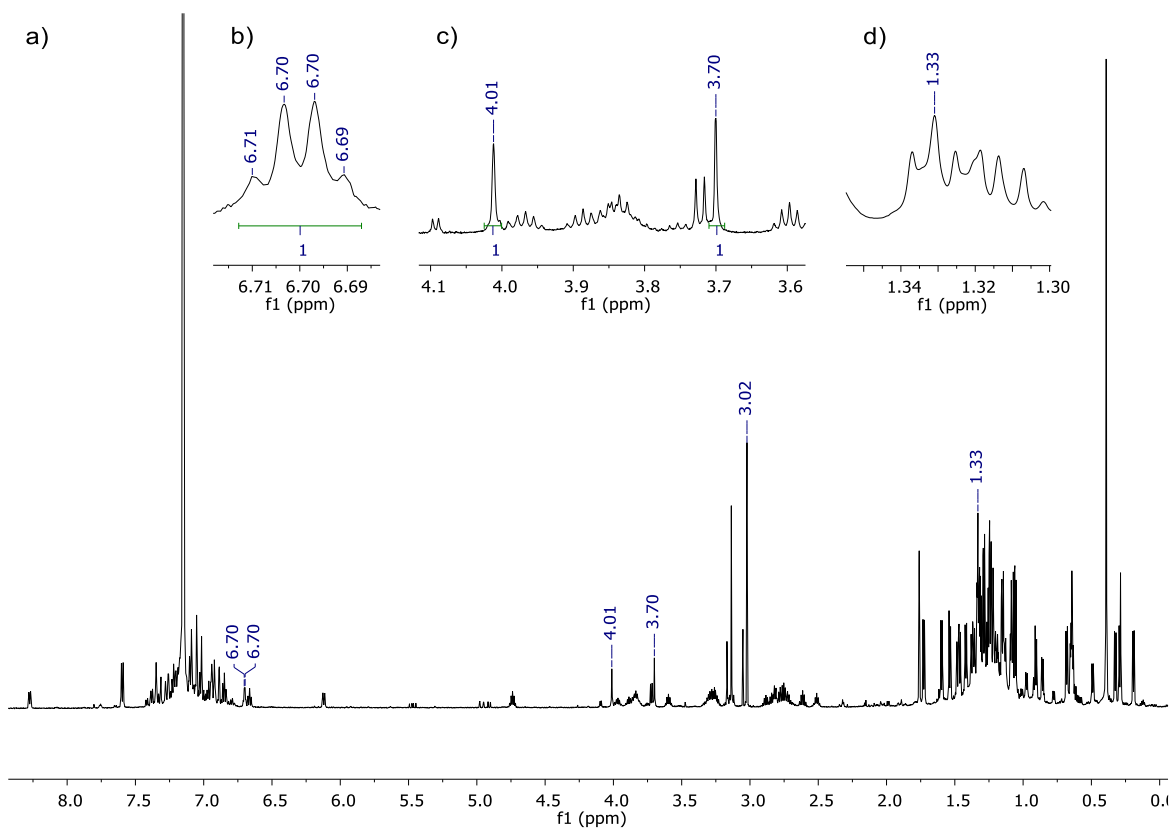


Figure 2.5: a) ^1H NMR spectrum of **2.11** (600 MHz, C_6D_6); b) Expansion from 6.69 – 6.71 ppm; c) Expansion from 3.6 – 4.1 ppm; d) Expansion from 1.30 – 1.35 ppm.

Two singlets were observed at 3.70 and 4.01 ppm in the ^1H NMR spectrum of **2.11**. The two singlets correlated to signals at 92.23 and 54.08 ppm in the ^{13}C dimension of the ^{13}C - ^1H gHSQC NMR spectrum of **2.11**, respectively. A strong correlation between

the two ^1H signals was also observed in the ^1H - ^1H gCOSY NMR spectrum. On the basis of the ^{13}C chemical shifts, as well as the strong correlation observed in the ^1H - ^1H gCOSY NMR spectrum, the singlets at 3.70 and 4.01 ppm were assigned to the CH-OMe and CH-Ph moieties, respectively. A correlation between the signal at 3.70 ppm in the ^1H dimension and signals at 17.59 ppm and 56.80 ppm in the ^{13}C dimension of the ^{13}C - ^1H gHMBC NMR spectrum of **2.11** were observed (Figure 2.6).

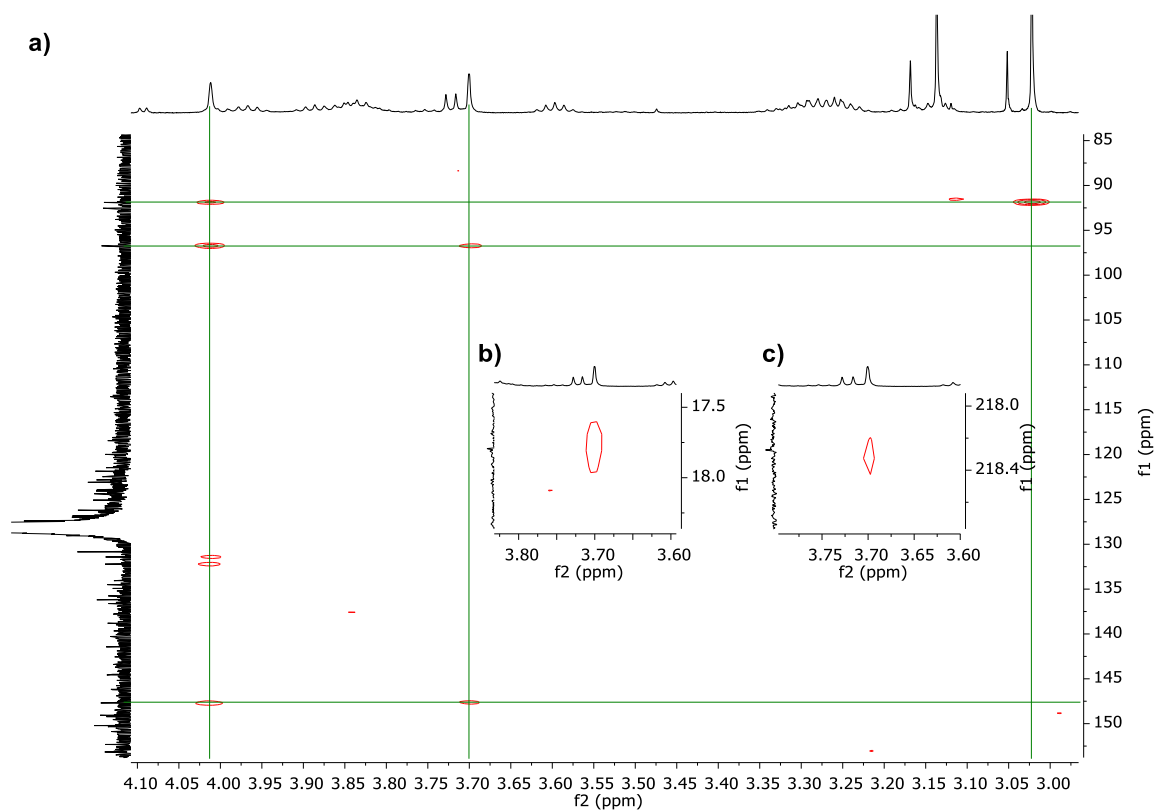


Figure 2.6: Expansion of the ^{13}C - ^1H gHMBC NMR spectrum of **2.11** (600 MHz, C_6D_6) with ^1H ranges of: a) 3.00-4.10 ppm; b) 3.60-3.80 ppm (^{13}C range of 17.5-18.0 ppm); c) 3.60-3.80 ppm (^{13}C range of 218.0-218.6 ppm);

The signal at 17.59 ppm correlated to a masked signal at 1.35 ppm in the ^1H dimension of the ^{13}C - ^1H gHSQC NMR spectrum while the ^{13}C signal at 56.80 ppm correlated to a ^1H singlet at 3.02 ppm. As such, the singlet at 1.33 ppm in the ^1H NMR spectrum was assigned to the methyl substituent derived from **1.31**, while the singlet at 3.02 ppm was assigned to the methoxy group on the basis of the chemical shifts and observed correlations in the ^{13}C - ^1H gHMBC NMR spectrum of **2.11**. The correlation critical to the elucidation of the structure of **2.11** was observed in the ^{13}C - ^1H gHMBC NMR spectrum between the signal at 3.70 ppm in the ^1H dimension and the signal at 218.32 ppm of the ^{13}C dimension. The signal at 218.32 ppm was assigned to an allenic carbon on the basis of the chemical shift and by comparison to the chemical shifts of the allenic carbon in **2.5** and **2.6** at 213.1 ppm and 210.2 ppm, respectively (Table 2.1). A correlation in the ^1H - ^1H gCOSY NMR spectrum of **2.11** between the signals at 1.33 ppm, assigned to the methyl substituent and 6.70 ppm was observed. The signal at 6.70 ppm also correlated to a signal at 92.32 ppm in the ^{13}C dimension of the ^{13}C - ^1H gHSQC NMR spectrum of **2.11**. By comparison of the correlations observed, as well as the analogous chemical shifts of **2.5** and **2.6**, the signals at 6.70 ppm and 92.32 ppm in the ^1H and ^{13}C NMR spectra, respectively, were assigned to the allenic moiety. These assignments led to the fragment presented in Chart 2.3.

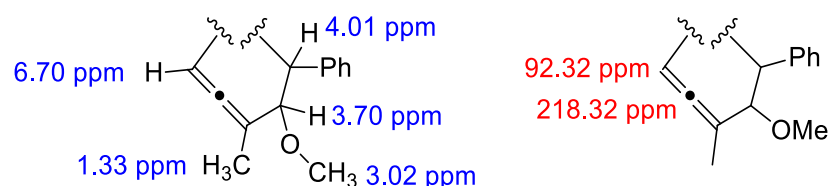


Chart 2.3: Fragments of **2.11** highlighting key ^1H signals in blue and key ^{13}C signals in red.

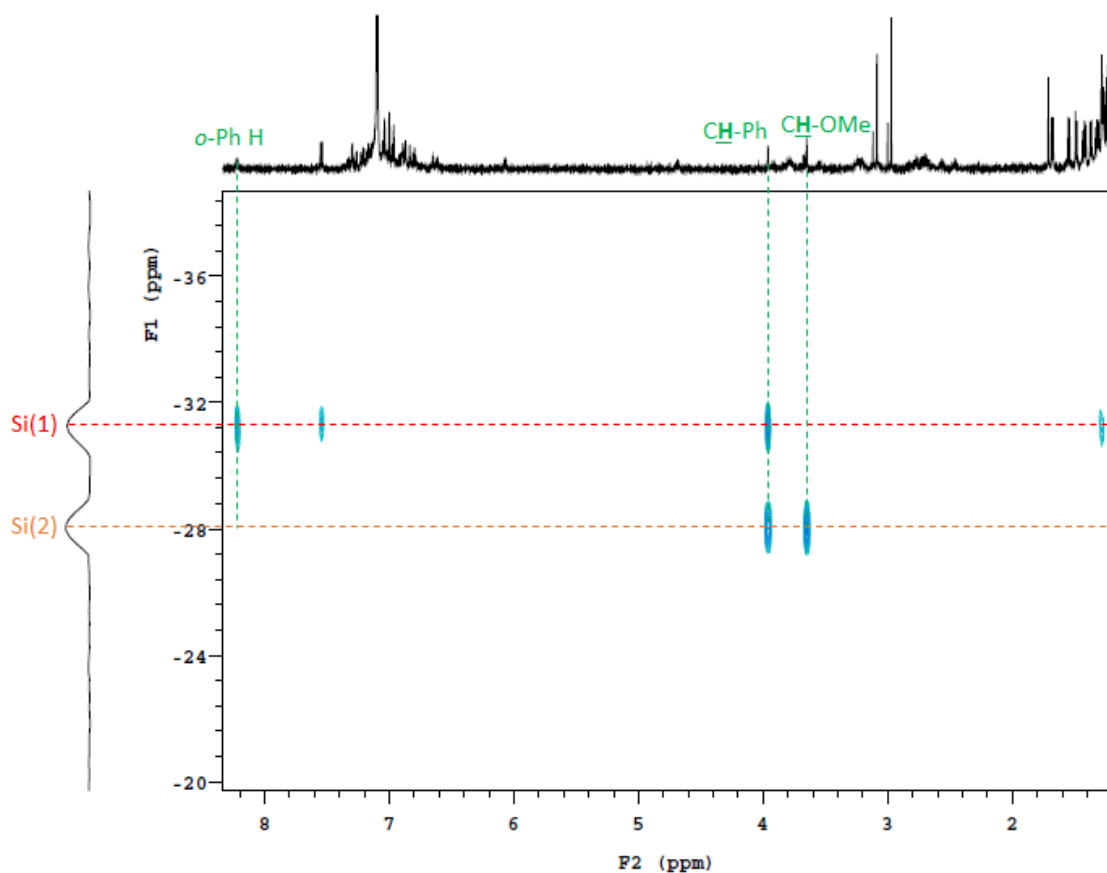


Figure 2.7: Expansion of the ^{29}Si - ^1H gHMBC NMR spectrum of **2.11** (600 MHz, C_6D_6). The signals at -31 and -28 ppm in the ^{29}Si dimension are noted as Si(1) and Si(2), respectively.

To determine the regiochemistry of the phenyl and methoxy substituents the ^{29}Si - ^1H gHMBC NMR spectrum of **2.11** was recorded. The resulting spectrum is illustrated in Figure 2.7. Similar correlations were observed in the ^{29}Si - ^1H gHMBC NMR spectra of **2.10** and **2.11**. The signal at -31 ppm in the ^{29}Si dimension of the ^{29}Si - ^1H gHMBC NMR spectrum of **2.11** correlated with a doublet in the ^1H dimension at 7.60 ppm, assigned to an *o*-Ph-H, and a singlet at 4.02 ppm in the ^1H dimension which was assigned to the CH-

Ph moiety of the ring. The other signal in the ^{29}Si dimension of the ^{29}Si - ^1H gHMBC NMR spectrum of **2.11**, at -28 ppm, correlated to both the $\underline{\text{CH}}$ -Ph and $\underline{\text{CH}}$ -OMe signals at 4.01 and 3.70 ppm, respectively, in the ^1H dimension. These correlations establish the regiochemistry of the phenyl and methoxy substituents on the seven-membered ring and the phenyl substituent of the disilane fragment to yield the final elucidated structure shown in Chart 2.4.

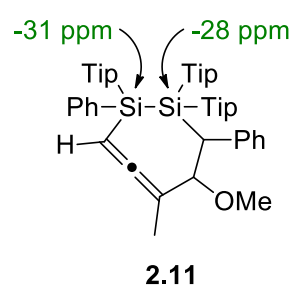


Chart 2.4: Elucidated structure of **2.11** highlighting key ^{29}Si signals in green.

Compound **2.12** was also identified and is the major compound in the ^1H NMR spectrum of the crude residue. The region from 2.5 – 4 ppm in the ^1H NMR spectrum of **2.12** is shown in Figure 2.8. The ESI mass spectrum of **2.12** revealed a signal at m/z 951.625 suggesting that **2.12** is an isomer of **2.10** and **2.11**.

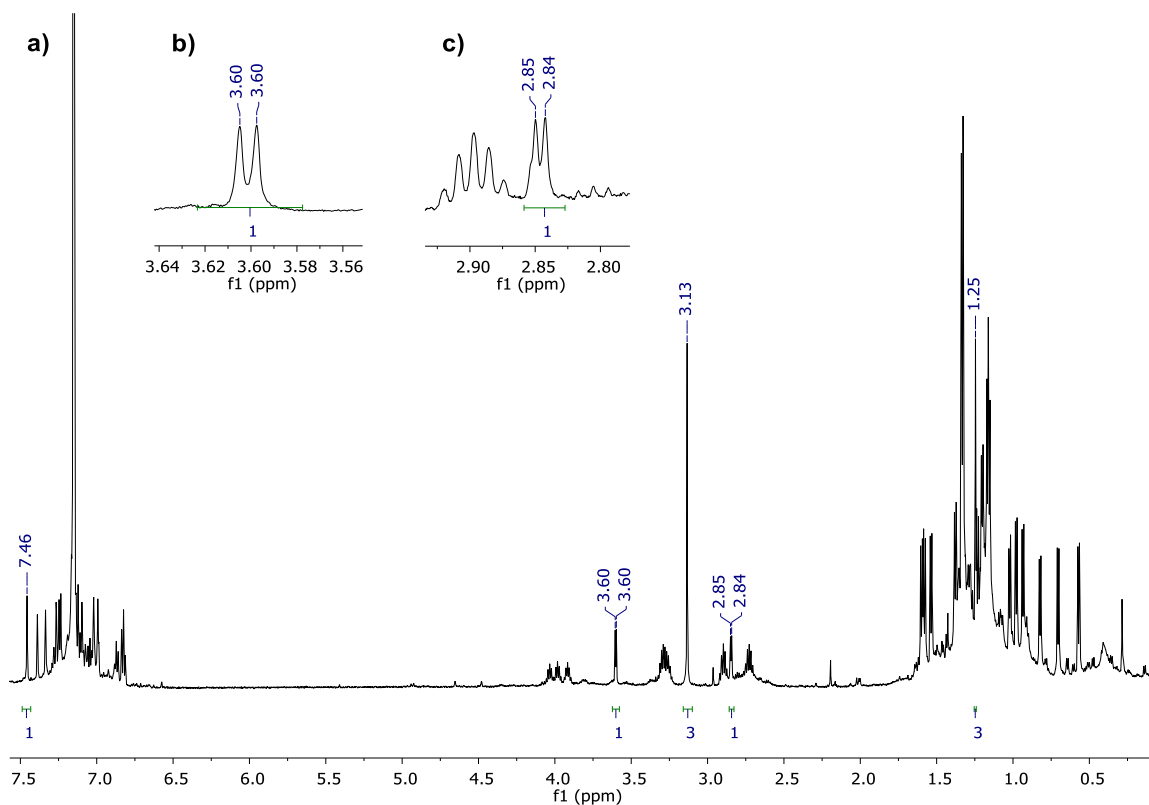
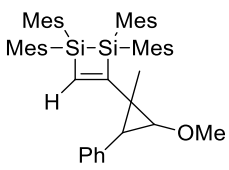
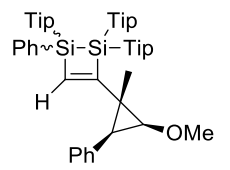
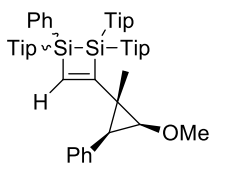


Figure 2.8: a) ^1H NMR spectrum of **2.12** (600 MHz, C_6D_6); b) Expansion from 3.56 – 3.64 ppm; c) Expansion from 2.80 – 2.90 ppm.

Once again, two doublets, at 2.84 and 3.60 ppm, in the ^1H NMR spectrum of **2.12** were found to correlate to signals at 41.24 ppm and 73.37 ppm in the ^{13}C dimension of the ^{13}C - ^1H gHSQC NMR spectrum of **2.12**, respectively, and thus, were assigned to CH-Ph and CH-OMe moieties. The ^1H - ^1H gCOSY NMR spectrum of **2.12** shows a correlation between these two signals with a coupling constant 4 Hz. The coupling constant is significantly different than the corresponding coupling constant in **2.10**. Furthermore, the chemical shifts of the signals at 2.84 and 3.60 ppm are similar to those assigned to the analogous hydrogens in compound **2.7** (Table 2.1). On the basis of these

data, the structure of compound **2.12** is a disilacyclobutene with the cyclopropyl ring intact.

Table 2.2: ^1H NMR and ^{13}C NMR chemical shifts of **2.7**, **2.12**, and **2.13**.

	 2.7	 2.12	 2.13
^1H NMR Chemical Shifts			
<u>H</u>CPh	2.31 [J = 5 Hz]	2.84 [J = 4 Hz]	2.65 [J = 4 Hz]
<u>H</u>COCH₃	3.98 [J = 5 Hz]	3.60 [J = 4 Hz]	3.79 [J = 4 Hz]
<u>CH</u>₃	1.60	1.25	1.59
O<u>CH</u>₃	3.17	3.13	3.26
C=<u>CH</u>	6.88	7.46	7.00
^{13}C NMR Chemical Shifts			
<u>H</u>CPh	43.06	41.24	39.42
<u>H</u>COCH₃	73.06	73.37	72.76
O<u>CH</u>₃	57.79	57.25	58.30
C_q	37.32	37.08	32.53

The signal at 37.08 ppm in the ^{13}C NMR spectrum of **2.12** was assigned to the quaternary carbon of the cyclopropyl ring by comparison with the chemical shift of the analogous carbon in compound **2.7** (37.32 ppm). The signal assigned to the quaternary carbon showed correlations to singlets in the ^1H dimension at 7.46 ppm and 1.25 ppm in the ^{13}C - ^1H gHMBC NMR spectrum of **2.12**.

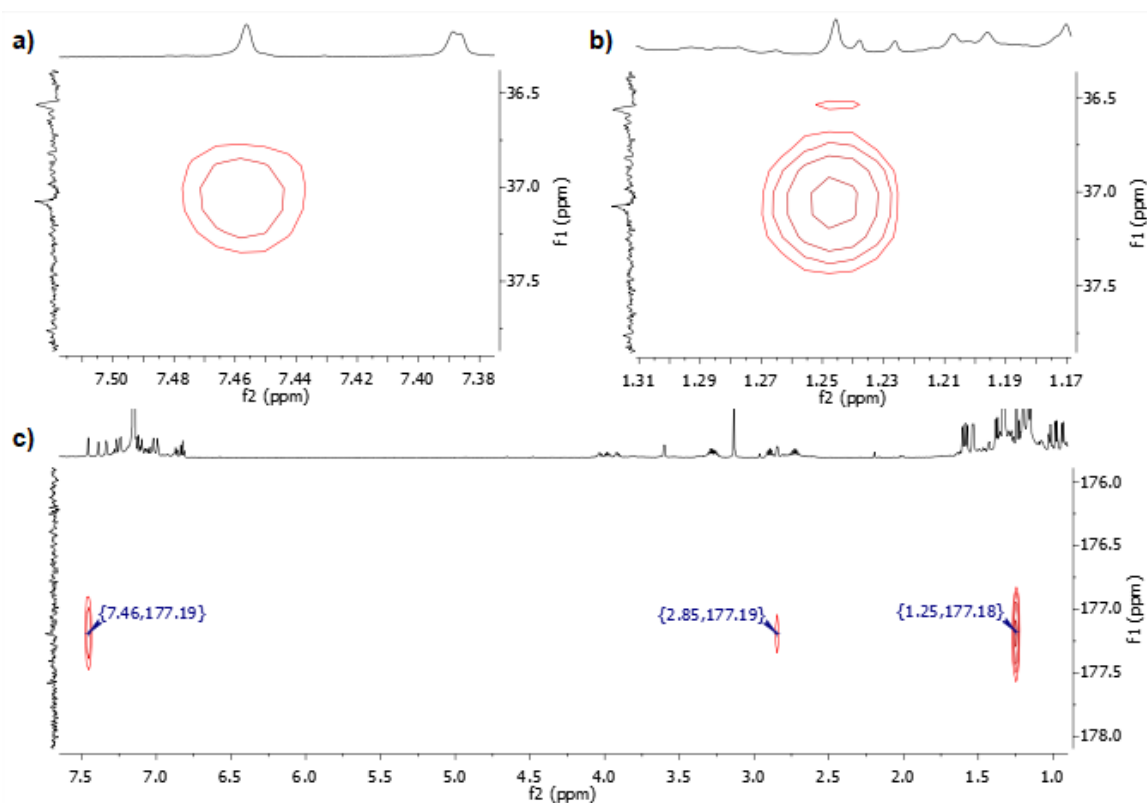


Figure 2.9: Expansion of the ^{13}C - ^1H gHMBC NMR spectrum of **2.12** (600 MHz, C_6D_6) with ^1H ranges of: a) 7.38-7.50 ppm (^{13}C range of 36.5-37.5 ppm); b) 1.17-1.31 ppm (^{13}C range of 36.5-37.5 ppm); c) 1.0-7.5 ppm (^{13}C range of 176.0-178.0 ppm);

The former correlated to a signal at 152.57 ppm in the ^{13}C dimension of the ^{13}C - ^1H gHSQC NMR spectrum of **2.12**, and was assigned to the vinylic hydrogen of the 4-

membered ring, while the latter was assigned to the methyl group of the cyclopropyl ring. Both singlets showed correlations to a quaternary carbon at 177.19 ppm in the ^{13}C dimension of the ^{13}C - ^1H gHMBC spectrum which was assigned to disubstituted vinylic carbon of the 4-membered ring. These data further support the assigned structure of **2.12**.

The ^{29}Si - ^1H gHMBC NMR spectrum of **2.12** showed two signals in the ^{29}Si dimension at -16 and -12 ppm (Figure 2.10).

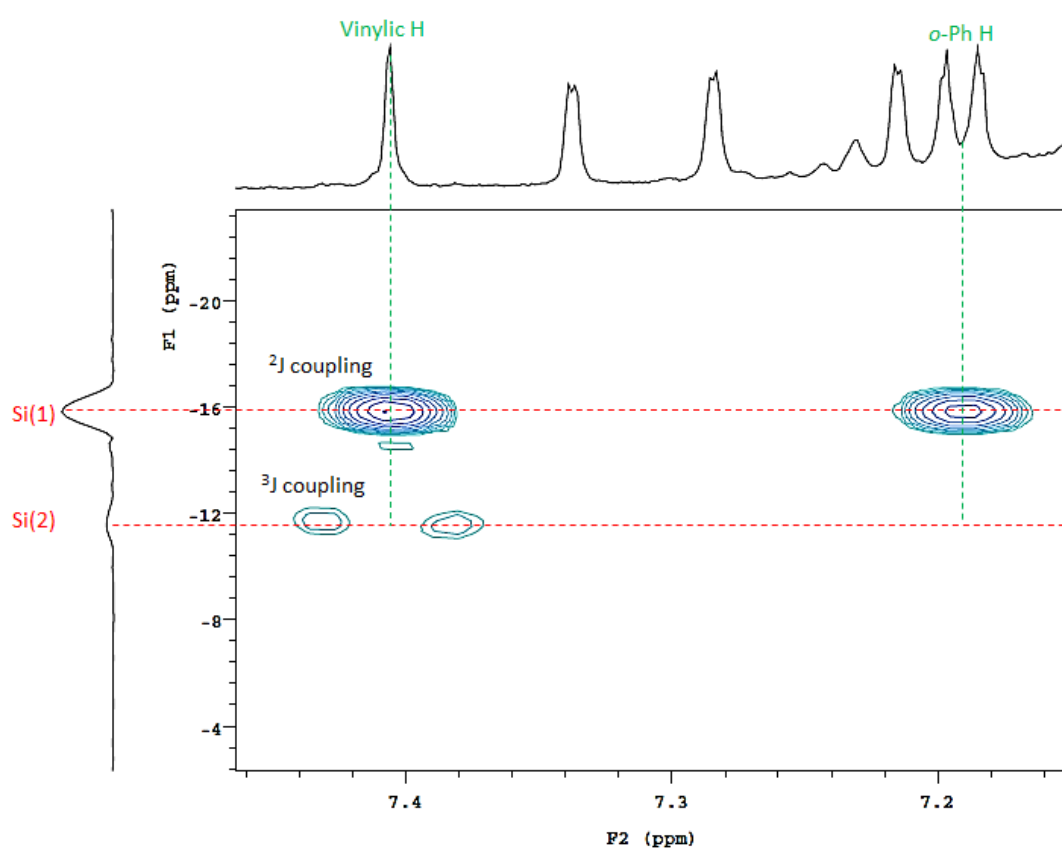
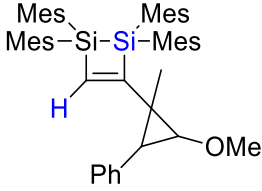
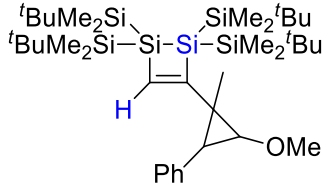



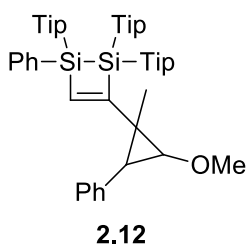
Figure 2.10: Expansion of the ^{29}Si - ^1H gHMBC NMR spectrum of **2.12** (600 MHz, C_6D_6). The signals at -16 and -12 ppm in the ^{29}Si dimension are noted as Si(1) and Si(2), respectively.

Correlations were observed between the signal at -16 ppm in the ^{29}Si dimension and a doublet at 7.24 ppm in the ^1H dimension which was assigned to an phenyl *ortho*-hydrogen. Since no similar correlation was observed to the signal at -12 ppm, the signal at -16 ppm was assigned to the silicon atom bearing the phenyl substituent. In addition, a correlation was observed between the signal at -16 ppm and the signal assigned to the vinylic hydrogen of the disilacyclobutene ring at 7.46 ppm in the ^1H dimension. The correlation was unresolved; however, is consistent with having a coupling constant estimated to be ~6 Hz, indicative of a 2-bond ^{29}Si - ^1H coupling in disilacyclobutenes (Table 2.3).¹⁰ The signal at -12 ppm in the ^{29}Si dimension also shows a correlation to the signal at 7.46 ppm with a coupling constant of 29 Hz. The magnitude of the coupling constant is indicative of a 3-bond ^{29}Si - ^1H coupling in disilacyclobutenes.¹⁰ As such, the unsubstituted vinylic carbon is bound to the silicon with a chemical shift of -16 ppm while the substituted vinylic carbon is bound to the silicon at -12 ppm.

Table 2.3: $^3J_{\text{Si-H}}$ coupling constants for known disilacyclobutene compounds

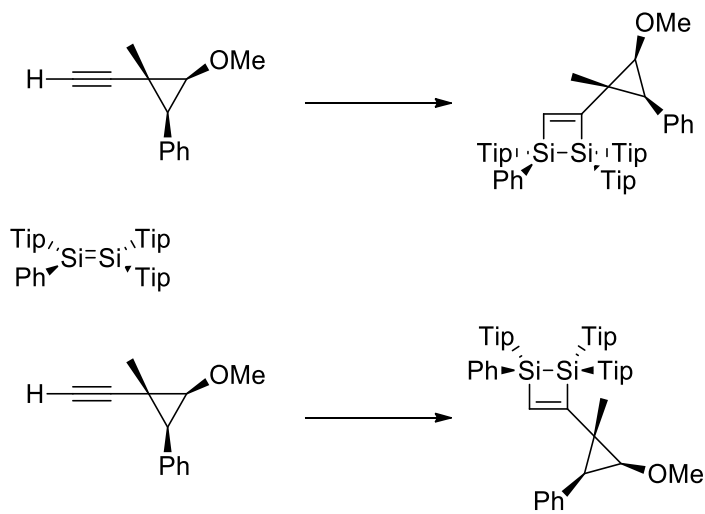
Disilacyclobutene	$^2J_{\text{Si-H}}$, Hz	$^3J_{\text{Si-H}}$, Hz	Reference
	7 Hz	30 Hz	7
	8 Hz	23 Hz	9
	-	29 Hz	3

On the basis of these data, the structure of **2.12** was elucidated as shown in Chart 2.5.

**Chart 2.5:** Elucidated structure for **2.12**.

The ^1H NMR spectrum of **2.13** was very similar to that of **2.12** and, as such, the analysis and elucidation of **2.13** was identical. The diagnostic signals for **2.13** are listed in Table 2.2. Due to correlations in the ^{29}Si - ^1H gHMBC NMR spectrum of **2.13** that are similar to

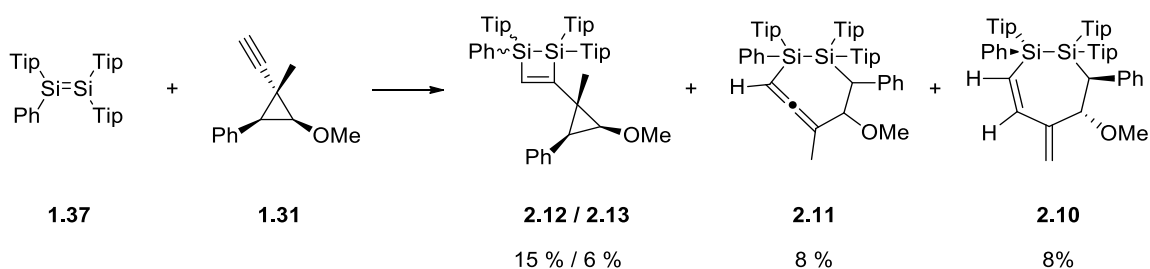
those observed with **2.12**, **2.13** was determined not to be a regioisomer of **2.12**; **2.12** and **2.13** are stereoisomers. While the difference in stereochemistry for **2.12** and **2.13** has not been unambiguously determined, we believe that the stereochemistry of the phenyl-substituted silicon differs giving rise to the two isomers (Scheme 2.7). The coupling constant between the two hydrogens on the cyclopropyl ring is 4 Hz for both **2.12** and **2.13** implying the hydrogens on the cyclopropyl ring are *trans* to one another; however, complete conversion of the stereochemistry of these hydrogens or the cyclopropyl ring of **1.31**, from *cis* to *trans*, seems implausible.



Scheme 2.7: The addition of alkyne **1.31** to **1.37** yielding two stereoisomers.

2.2.2 Mechanistic Insights

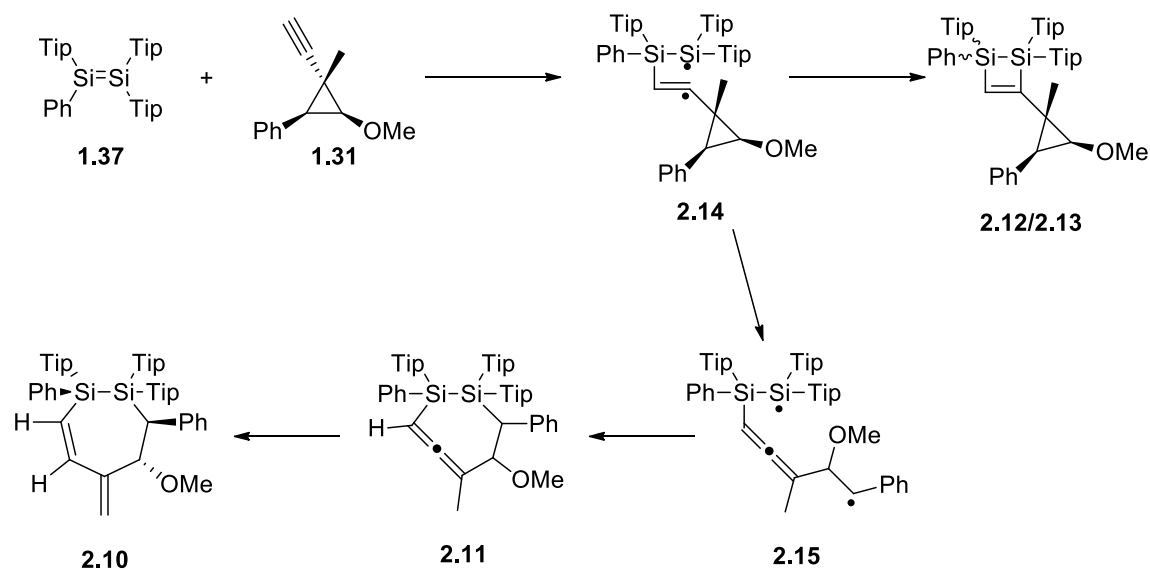
Upon addition of the cyclopropyl alkyne probe **1.31** to disilene **1.37**, compounds **2.12** and **2.13**, featuring a 4-membered ring, and **2.10** and **2.11**, featuring a 7-membered ring, were formed (Scheme 2.8). In all four isolated compounds, the less hindered carbon of the alkyne **1.31** adds to the less hindered silicon of disilene **1.37**, the silicon with a phenyl substituent.



Scheme 2.8: The reaction of disilene **1.31** with alkyne **1.37**. Isolated yields are shown under the compound numbers.

Our results are consistent with those reported by Scheschkewitz for the addition of phenylacetylene to disilenes **1.37** and **1.5** where the terminal end of the alkyne is attached to the less sterically hindered silicon (Scheme 2.2). In compounds **2.10** and **2.11**, the phenyl substituent derived from **1.31** is located α to the nearest silicon, whereas the methoxy substituent is located β to the nearest silicon. The regiochemistry of the phenyl and methoxy substituents in compounds **2.10** and **2.11** provide strong evidence for the formation of a biradical intermediate during the addition of alkyne **1.31** to disilene **1.37**. The mechanism for the formation of **2.10-2.13** is illustrated in Scheme 2.9. Addition of

1.31 results in the formation of biradical **2.14**. Regioselective ring-opening towards the phenyl substituent results in the formation of the biradical **2.15**. Ring closure in **2.15** generates the 7-membered-ring allene **2.11**. A hydrogen shift from the methyl to the central allenic carbon gives **2.10**.

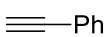
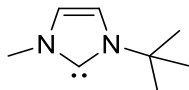
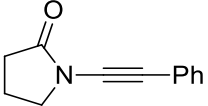
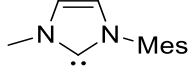
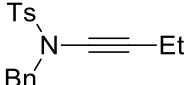
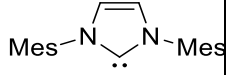


Scheme 2.9: Mechanism of the reaction between cyclopropyl alkyne probe **1.31** and **1.37**.

The mechanism for the reaction of alkyne **1.31** with disilene **1.37** and **1.4** proceeds through a biradical intermediate in each case. This is not surprising given both are tetraaryl-substituted disilenes. Our results are not consistent with the proposal suggested by Scheschkewitz: that addition of an alkyne to a polarized disilene will proceed through a zwitterionic intermediate. Scheschkewitz based his hypothesis on two assumptions: 1) disilene **1.37** is polarized, and 2) the formation of stable dipolar intermediates observed upon coordination of an NHC to a disilene.⁶ We believe that the

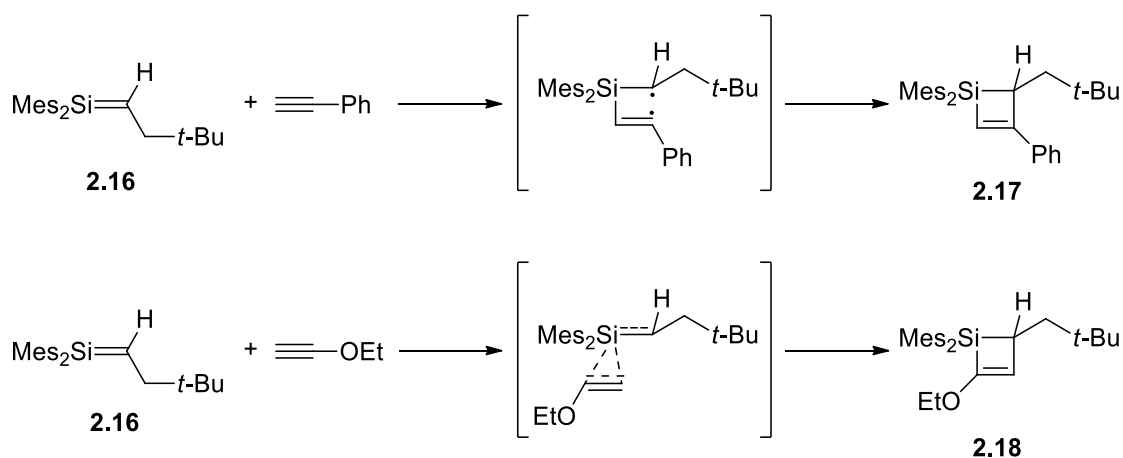
polarization of the Si=Si bond in **1.37** with one phenyl and three triisopropylphenyl substituents is not sufficient to change the reaction pathway from one favouring a biradical intermediate to one favouring a zwitterionic intermediate. The nature of the reagent plays a critical role in a reaction mechanism. Scheschkewitz made the assumption the mechanism of the addition of an alkyne to a disilene will be comparable to that of an NHC. However, NHCs are far better nucleophiles/donors compared to alkynes as established quantitatively by the Mayr-Patz equation and listed in Table 2.4.^{11,12} The higher the nucleophilicity parameter N , the better the nucleophile. As such alkynes are weak nucleophiles while NHCs are strong nucleophiles. Therefore, the comparison made by Scheschkewitz, is not valid.

Table 2.4: Literature reported nucleophile-specific parameters for various alkynes and NHC compounds.

Compound	Solvent	$N (s_N)$ value	Compound	Solvent	$N (s_N)$ value
	CH ₂ Cl ₂	-0.04 (0.77)		THF	16.54 (0.47)
	CH ₂ Cl ₂	3.12 (0.85)		THF	21.50 (0.45)
	CH ₂ Cl ₂	5.16 (0.85)		THF	21.72 (0.80)

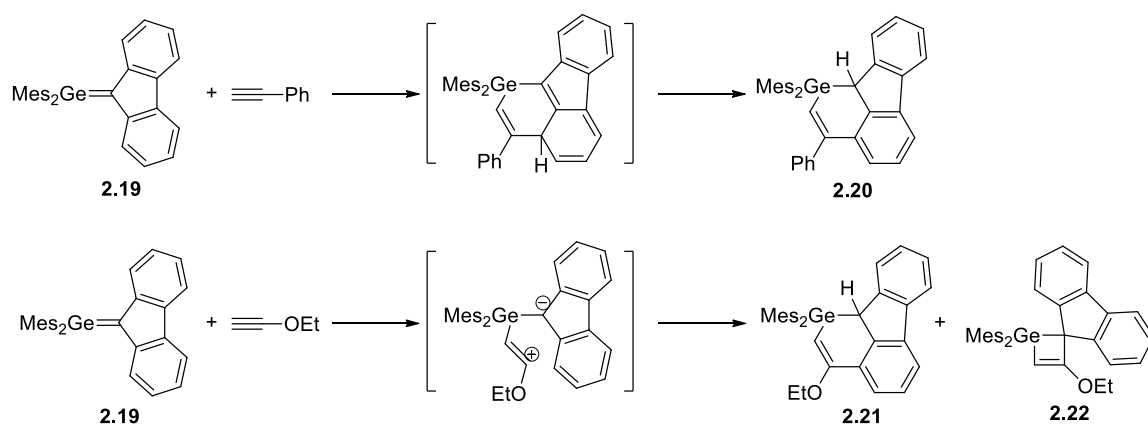
While the nature of the intermediate in the reaction between an alkyne and a disilene has not been altered by changing the disilene substituents to polarize the Si=Si

double bond, it has been reported that changing the substituents on the alkyne has altered the reaction mechanism.¹³ For instance, in addition of phenylacetylene to silene **2.16** (Scheme 2.10), the silacyclobutene **2.17** was observed. It was concluded, on the basis of computational results, that the addition was initiated with the formation of the Si-C bond, between the silenic silicon and the unsubstituted carbon of the alkynyl, and proceeded through a biradical intermediate. Similar products were observed with the addition of 1-ethynyl-4-(trifluoromethyl)benzene and 4-ethynylanisole to silene **2.16**. In contrast, the addition of ethoxyacetylene to silene **2.16** (Scheme 2.10) formed silacyclobutene **2.18** which has the opposite regiochemistry compared to the silacyclobutenes formed from the arylalkynes. The reaction between **2.16** and the ethoxyacetylene was proposed to proceed through a concerted mechanism via a hypercoordinated transition state. Thus, the mechanism of the reaction was clearly influenced by the substituent on the alkyne.



Scheme 2.10: Addition of phenylacetylene and ethoxyacetylene to silene **2.16**.

Similarly, the addition of alkynes to the fluorylidene germane **2.19** showed a comparable result.¹⁴ While the addition of phenylacetylene to **2.19** resulted in the formation of the cycloadduct, **2.20**; the addition of ethoxyacetylene to **2.19**, while producing the analogous cycloadduct **2.21**, also generated germacyclobutene **2.22** (Scheme 2.11). Interestingly, the regiochemistry of the ethoxyacetylene addition in **2.22** is opposite to that observed in the addition of ethoxyacetylene to **2.19**. DFT calculations suggest that the reaction proceeds through a zwitterionic pathway where the negative charge would be stabilized by delocalization through the fluorenyl group and the positive charge would be stabilized by the ethoxy group.¹⁴



Scheme 2.11: Addition of phenylacetylene and ethoxyacetylene to germene **2.19**.

2.3 Conclusions

In summary, the addition of **1.31** to **1.37** was examined. The reaction yielded compounds **2.10-2.13** and their structures were elucidated by both one-dimensional and

two-dimensional NMR spectroscopy, mass spectrometry, and X-ray crystallography. Of the identified compounds, two compounds, **2.12** and **2.13**, were isomeric disilacyclobutenes, and the other two compounds, **2.10** and **2.11** were isomeric seven-membered ring compounds. Compound **2.11** is an allene and **2.10** appears to be derived from **2.11** from a rearrangement which occurs during isolation. The regiochemistry of the phenyl and methoxy substituents originating from **1.31**, in **2.10** and **2.11** with phenyl substituent α to the nearest silicon atom reveals that the addition of **1.31** to the asymmetrically-substituted disilene **1.37** proceeds through a biradical intermediate. The structures of **2.10** and **2.11** are consistent with the analogous products, **2.5** and **2.6**, and the results contradict Scheschkewitz's proposal of a zwitterionic intermediate in the addition of an alkyne to an asymmetrically substituted disilene.^{3,7}

The mechanism for the addition of alkynes to disilenes using alkyne **1.31** as a mechanistic probe has been studied for three different disilenes: the symmetrically-substituted tetraaryldisilene **1.4**, the symmetrically-substituted tetrasilyldisilene **1.29**, and the asymmetrically-substituted tetraaryldisilene **1.37**. For all cases, the addition has been determined to proceed through a biradical intermediate. The proposed intermediate by Scheschkewitz was based on the observation of a stable dipolar intermediate formed from the reaction of an asymmetrically-substituted disilene and an NHC. However, in comparison to an alkyne an NHC is a much stronger nucleophile, and thus, the comparison was not valid.

2.4 Experimental

2.4.1 General Procedure

All reactions were conducted under a nitrogen atmosphere using an MBraun Labmaster 130 glovebox. Pre-coated silica glass plates suitable for preparative thin-layer chromatography were purchased from Millipore Sigma. Solvents and reagents were purified by standard methods.¹⁵ Disilene **1.37** was obtained from Prof. Dr. D. Scheschkewitz, Saarland University. Cyclopropyl alkyne **1.31** was synthesized by Nada Tashkandi in the Baines lab.

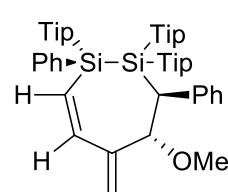
¹H and ¹³C NMR data were obtained on a 600 MHz INOVA NMR spectrometer. The standards used were as follows: residual C₆D₅H (7.15 ppm) for ¹H NMR spectra; C₆D₆ (128.00 ppm) and (29.80 ppm) for ¹³C NMR spectra. J values are reported in Hertz. ESI mass spectra were recorded on a Bruker microTOF II mass spectrometer with an electrospray interface in positive ion mode (reported in mass-to-charge units, *m/z*).

2.4.2 Addition of Probe **1.31** to Asymmetric Disilene **1.37**

Disilene **1.37** (180 mg, 0.24 mmol) and alkyne **1.31** (44 mg, 0.24 mmol) were dissolved in hexanes (~10 mL) to give a deep red-orange solution. The mixture was allowed to stir

for 18 h. During this time, the deep red-orange colour of the solution faded to orange with a pale-yellow precipitate. The precipitate was removed by centrifugation before the solvent was removed *in vacuo* (mass recovery = 96.5%). The ^1H NMR spectrum of the crude mixture revealed the presence of compounds **2.11**, **2.12**, and **2.13** in a ratio of 1.0 : 0.8 : 1.5, respectively. During preparation for TLC, the mixture was dissolved in DCM under the ambient atmosphere which caused a colour change from red to colourless. After separation of the sample by preparative TLC (hexanes: CH_2Cl_2 , 70:30), compounds **2.10** – **2.12** were obtained. Approximately 40% of the sample applied to the plate was recovered.

Compound 2.10



Yield = 8%, ^1H NMR (C_6D_6 , 600 MHz): δ = 8.16 (d, J = 7.6 Hz, 1 H, *o*-Ph-H), 7.31 - 6.66 (m, 9 H, Ph-H), 7.29 (m, 1 H, *m*-Tip-H), 7.12 (d, J = 16 Hz, 1 H, Si-CH=C), 7.11 (d, J = 1.6 Hz, 1 H, *m*-Tip-H), 7.04 (d, J = 1.6 Hz, 1 H, *m*-Tip-H), 7.00 (d, J = 1.6 Hz, 1 H, *m*-Tip-H), 6.93 (d, J = 1.6 Hz, 1 H, *m*-Tip-H), 6.73 (d, J = 16 Hz, 1 H, C=CH-C), 6.58 (d, J = 1.6 Hz, 1 H, *m*-Tip-H), 4.93 (d, J = 10 Hz, 1 H, CH-Ph), 4.66 (s, 1 H, C=CH₂), 4.48 (s, 1 H, C=CH₂), 4.36 (sept, J = 6.6 Hz, 1 H, ^{*i*}Pr CH), 4.08 (d, J = 10 Hz, 1 H, CH-OMe), 3.88 (sept, J = 6.6 Hz, 1 H, ^{*i*}Pr CH), 3.62 (sept, J = 6.6 Hz, 1 H, ^{*i*}Pr CH), 3.56 (m, 1 H, ^{*i*}Pr CH), 3.34 (sept, J = 6.6 Hz, 1 H, ^{*i*}Pr CH), 2.82-2.70 (m, 4 H, ^{*i*}Pr CH), 2.20 (s, 3 H, CH₃) 1.65 (d, J = 6.4 Hz, 3 H, ^{*i*}Pr CH₃), 1.62 (d, J = 6.4 Hz, 3 H, ^{*i*}Pr CH₃), 1.46 (d, J = 6.4 Hz, 3 H, ^{*i*}Pr CH₃), 1.46 (d, J = 6.4 Hz, 3 H, ^{*i*}Pr CH₃), 1.34 (d, J = 6.4 Hz, 3 H, ^{*i*}Pr CH₃), 1.28 (d, J = 6.4 Hz, 6 H, ^{*i*}Pr CH₃), 1.24 (d, J = 6.4 Hz, 3 H, ^{*i*}Pr CH₃), 1.18 (d, J = 6.4 Hz, 3 H, ^{*i*}Pr CH₃), 1.17 (d, J =

6.4 Hz, 3 H, ⁱPr CH₃), 1.10 (d, $J = 6.4$ Hz, 3 H, ⁱPr CH₃), 1.08 (d, $J = 6.4$ Hz, 3 H, ⁱPr CH₃), 1.02 (d, $J = 6.4$ Hz, 3 H, ⁱPr CH₃), 0.79 (d, $J = 6.4$ Hz, 3 H, ⁱPr CH₃), 0.65 (d, $J = 6.4$ Hz, 3 H, ⁱPr CH₃), 0.61 (d, $J = 6.4$ Hz, 3 H, ⁱPr CH₃), 0.48 (d, $J = 6.4$ Hz, 3 H, ⁱPr CH₃), 0.36 (d, $J = 6.4$ Hz, 3 H, ⁱPr CH₃), 0.15 (d, $J = 6.4$ Hz, 3 H, ⁱPr CH₃). ¹³C NMR (151 MHz, C₆D₆) $\delta = 155.57, 155.31, 154.76, 154.27, 154.16, 152.76, 149.41, 149.15, 148.13, 145.21, 143.44, 141.27, 139.73, 138.48, 137.93, 135.08, 127.98, 127.77, 126.68, 125.67, 125.18, 124.73, 124.64, 123.96, 123.89, 123.27, 123.19, 123.02, 122.95, 122.63, 122.57, 122.45, 120.03, 91.24, 67.83, 57.42, 37.85, 37.83, 37.76, 35.82, 35.76, 35.69, 35.59, 34.55$ (br), 30.79, 30.66, 26.71, 26.66, 26.16, 25.95, 25.82, 25.71, 25.55, 25.50, 24.80, 24.78, 24.10 (br), 23.41, 23.36, 21.01, 20.99. ²⁹Si-¹H gHMBC NMR (C₆D₆, 119 MHz): $\delta = -12$ (SiTip₂), -32 (SiPhTip). ESI-MS: m/z 951.6279 (calcd for C₆₄H₈₈NaOSi₂, 951.6271).

Data Collection and Processing. The sample (n18010) was submitted by Andrew Henry of the Baines research group at the University of Western Ontario and run by Jeremy Bourque. The sample was mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Nonius Bruker KappaCCD Apex2 diffractometer at a temperature of 110 K. The unit cell dimensions were determined from a symmetry constrained fit of 9995 reflections with $7.12^\circ < 2\theta < 128.02^\circ$. The data collection strategy was a number of ω and χ scans which collected data up to 128.808° (2θ). The frame integration was performed using SAINT.¹⁶ The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.¹⁷

Structure Solution and Refinement. The structure was solved by using a dual space methodology using the SHELXT program.¹⁸ All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. Several regions of disorder were found at the *para* isopropyl groups of the Tip ligands. Most involved an inversion at the methine carbon of the isopropyl groups and refined to various normalized occupancies (0.607(12) for C23; 0.545(11) for C87'; 0.65(3) for C11A). The structural model was fit to the data using full matrix least-squares based on F^2 . The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL-2014 program from the SHELXTL suite of crystallographic software.¹⁹ Graphic plots were produced using the XP program suite.²⁰ Additional information and other relevant literature references can be found in the reference section of this website (<http://xray.chem.uwo.ca>).

Table 2.5: Summary of Structural Parameters for **2.10**.

Formula	C ₆₄ H ₈₈ OSi ₂
Formula Weight (g/mol)	929.52
Crystal Dimensions (mm)	0.309 × 0.214 × 0.134
Crystal Color and Habit	colourless prism
Crystal System	triclinic
Space Group	P -1
Temperature, K	110
a , Å	11.657(2)
b , Å	22.035(4)
c , Å	24.824(4)
α , °	64.488(9)
β , °	77.996(10)
γ , °	81.660(7)
V , Å ³	5617.9(18)
Number of reflections to determine final unit cell	9995
Min and Max 2 θ for cell determination, °	7.12, 128.02
Z	4

F(000)	2032
ρ (g/cm)	1.099
λ , Å, (CuK α)	1.54178
μ , (cm ⁻¹)	0.858
Diffractometer Type	Nonius Bruker KappaCCD Apex2
Scan Type(s)	phi and omega scans
Max 2 θ for data collection, °	128.808
Measured fraction of data	0.985
Number of reflections measured	69911
Unique reflections measured	18577
R _{merge}	0.0646
Number of reflections included in refinement	18577
Cut off Threshold Expression	I > 2sigma(I)
Structure refined using	full matrix least-squares using F ²
Weighting Scheme	w=1/[sigma ² (Fo ²)+(0.0622P) ² +2.8121P] where P=(Fo ² +2Fc ²)/3
Number of parameters in least-squares	1246
R ₁	0.0527
wR ₂	0.1295
R ₁ (all data)	0.0724
wR ₂ (all data)	0.1419
GOF	1.048
Maximum shift/error	0.001
Min & Max peak heights on final ΔF Map (e ⁻ /Å)	-0.392, 0.447

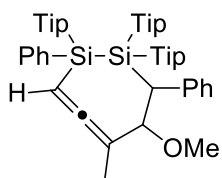
Where:

$$R_1 = \sum (|F_o| - |F_c|) / \sum F_o$$

$$wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w F_o^4)]^{1/2}$$

$$GOF = [\sum (w(F_o^2 - F_c^2)^2) / (\text{No. of reflns.} - \text{No. of params.})]^{1/2}$$

Compound 2.11

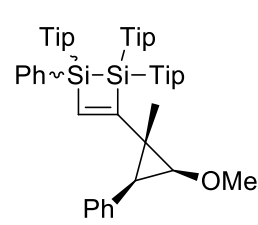


Compound **2.11** could not be fully isolated and still contains impurities. Yield = 8%, ¹H NMR (C₆D₆, 600 MHz): δ = 8.28 (d, 1 H, *o*-Ph-**H**), 7.63 – 6.12 (m, 9 H, Ph-**H**), 7.36 (d, *J* = 1.9 Hz, 1 H, *m*-Tip-**H**), 7.27 (m, 1 H, *m*-Tip-**H**), 7.10 (s, 1 H, *m*-Tip-**H**), 7.06 (s, 1 H, *m*-Tip-**H**), 7.27 (d, *J* =

H), 7.27 (m, 1 H, *m*-Tip-**H**), 7.10 (s, 1 H, *m*-Tip-**H**), 7.06 (s, 1 H, *m*-Tip-**H**), 7.27 (d, *J* =

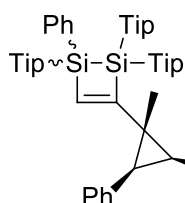
1.9 Hz, 1 H, *m*-Tip-**H**), 6.93 (d, $J = 1.9$ Hz, 1 H, *m*-Tip-**H**), 6.90 (d, $J = 1.9$ Hz, 1 H, *m*-Tip-**H**), 6.71 (q, $J = 3.5$ Hz, 1 H, Si-**CH=C**), 4.75 (sept, $J = 6.4$ Hz, 1 H, *i*Pr **CH**), 4.02 (s, 1 H, **CH-Ph**), 3.93 - 6.80 (m, 2 H, *i*Pr **CH**), 3.71 (s, 1 H, **CH-OMe**), 3.61 (sept, $J = 6.4$ Hz, 1 H, *i*Pr **CH**), 3.36 - 3.22 (m, 2 H, *i*Pr **CH**), 3.15 (m, 1 H, *i*Pr **CH**), 3.02 (s, 3 H, O**CH**₃), 2.76 (m, 1 H, *i*Pr **CH**), 2.52 (sept, $J = 6.4$ Hz, 1 H, *i*Pr **CH**), 1.74 (d, $J = 6.9$ Hz, 3 H, *i*Pr **CH**₃), 1.61 (d, $J = 6.9$ Hz, 3 H, *i*Pr **CH**₃), 1.55 (d, $J = 6.9$ Hz, 3 H, *i*Pr **CH**₃), 1.47 (d, $J = 6.9$ Hz, 3 H, *i*Pr **CH**₃), 1.43 (d, $J = 6.9$ Hz, 3 H, *i*Pr **CH**₃), 1.37 (d, $J = 6.9$ Hz, 3 H, *i*Pr **CH**₃), 1.33 (s, 3 H, **CH**₃), 1.33 (m, 3 H, *i*Pr **CH**₃), 1.30 (m, 3 H, *i*Pr **CH**₃), 1.25 (m, 6 H, *i*Pr **CH**₃), 0.92 (d, $J = 6.9$ Hz, 3 H, *i*Pr **CH**₃), 1.74 (d, $J = 6.9$ Hz, 3 H, *i*Pr **CH**₃), 0.69 (d, $J = 6.9$ Hz, 3 H, *i*Pr **CH**₃), 0.66 (d, $J = 6.9$ Hz, 3 H, *i*Pr **CH**₃), 0.65 (d, $J = 6.9$ Hz, 3 H, *i*Pr **CH**₃), 0.34 (d, $J = 6.9$ Hz, 3 H, *i*Pr **CH**₃), 0.30 (d, $J = 6.9$ Hz, 3 H, *i*Pr **CH**₃), 0.20 (d, $J = 6.9$ Hz, 3 H, *i*Pr **CH**₃). ¹³C NMR (151 MHz, C₆D₆) $\delta = 156.75, 154.59, 153.21, 152.38, 150.27, 149.28, 149.12, 147.75, 144.63, 141.50, 138.86, 136.25, 134.56, 132.28, 131.48, 130.91, 127.61, 127.45, 127.05, 126.90, 126.26, 126.22, 125.14, 124.43, 124.12, 123.98, 123.16, 122.89, 121.91, 120.04, 92.60, 57.11, 54.37, 37.96, 37.84, 36.17, 35.53, 35.18, 34.81, 34.75, 34.62, 34.51, 34.46, 34.33, 34.11, 29.25, 28.24, 27.87, 26.67, 26.59, 26.49, 26.45, 26.12, 25.80, 25.64, 25.27, 25.15, 24.89, 24.08$ (br) 23.49, 22.23, 17.87. ²⁹Si-¹H gHMBC NMR (C₆D₆, 119 MHz): $\delta = -28$ (**Si**Tip₂), -31 (**Si**PhTip). ESI-MS: m/z 951.6272 (calcd for C₆₄H₈₈NaOSi₂, 951.6271).

Compound 2.12



Yield = 15% ^1H NMR (C_6D_6 , 600 MHz): δ = 7.46 (s, 1 H, Si-CH=C), 7.40 (d, J = 1.5 Hz, 1 H, *m*-Tip-H), 7.34 (d, J = 1.5 Hz, 1 H, *m*-Tip-H), 7.30 – 6.82 (m, 9 H, Ph-H), 7.27 (d, J = 1.5 Hz, 1 H, *m*-Tip-H), 7.25 (d, J = 6.4 Hz, 1 H, *o*-Ph-H), 7.10 (d, J = 1.5 Hz, 1 H, *m*-Tip-H), 7.02 (d, J = 1.5 Hz, 1 H, *m*-Tip-H), 6.99 (d, J = 1.5 Hz, 1 H, *m*-Tip-H), 4.04 (sept, J = 6.5 Hz, 1 H, *i*Pr CH), 3.99 (sept, J = 6.5 Hz, 1 H, *i*Pr CH), 3.93 (sept, J = 6.5 Hz, 1 H, *i*Pr CH), 3.60 (d, J = 4.7 Hz, 1 H, CH-OMe), 3.34-3.24 (m, 3 H, *i*Pr CH), 3.13 (s, 3 H, OCH₃), 2.91 (sept, J = 6.5 Hz, 1 H, *i*Pr CH), 2.84 (d, J = 4.1 Hz, 1 H, CH-Ph), 2.74 (sept, J = 6.5 Hz, 2 H, *i*Pr CH), 1.60 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 1.59 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 1.55 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 1.38 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 1.34 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 1.34 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 1.34 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 1.25 (s, 3 H, CH₃), 1.24 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 1.22 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 1.17 (m, 9 H, *i*Pr CH₃), 1.03 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 0.99 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 0.83 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 0.71 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 0.58 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 0.34 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 0.25 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 0.16 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃), 0.07 (d, J = 6.8 Hz, 3 H, *i*Pr CH₃). ^{13}C NMR (151 MHz, C_6D_6) δ = 177.41, 156.97, 156.32, 156.26, 155.87, 154.79, 154.42, 150.71, 150.38, 150.23, 140.05, 138.29, 138.00, 136.58, 129.37, 129.29, 127.55, 122.95 (br), 120.02, 73.37, 57.70, 41.47, 37.31, 36.79, 36.33, 35.65, 35.02, 34.93, 34.73, 27.09, 25.86, 25.30, 24.83, 24.50 (br), 22.31, 22.09, 20.77. ^{29}Si - ^1H gHMBC NMR (C_6D_6 , 119 MHz): δ = -12 (SiTip₂), -16 (SiPhTip). ESI-MS m/z 951.6279 (calcd for $\text{C}_{64}\text{H}_{88}\text{NaOSi}_2$, 951.6271).

Compound 2.13



Yield = 6% ^1H NMR (C_6D_6 , 600 MHz): δ = 7.48 (d, J = 7.6 Hz, 1 H, *o*-Ph-H), 7.35 (d, J = 1.8 Hz, 1 H, *m*-Tip-H), 7.32 (d, J = 1.8 Hz, 1 H, *m*-Tip-H), 7.25 (d, J = 1.8 Hz, 1 H, *m*-Tip-H), 7.20 - 6.85 (m, 9 H, Ph-H), 7.19 (s, 1 H, *m*-Tip-H), 7.12 (d, J = 1.8 Hz, 1 H, *m*-Tip-H), 7.08 (m, 1 H, J = 7.0 Hz, *m*-Tip-H), 7.00 (s, 1 H, HC=C), 3.94 (sept, J = 6.4 Hz, 1 H, ^iPr CH), 3.80 (masked d, 1 H, CH-OMe), 3.75 (sept, J = 6.4 Hz, 1 H, ^iPr CH), 3.63 (br sept, 1 H, ^iPr CH), 3.38 (m, 1 H, ^iPr CH), 3.26 (s, 3 H, OCH₃), 3.24 (sept, J = 6.4 Hz, 1 H, ^iPr CH), 3.21 (sept, J = 6.4 Hz, 1 H, ^iPr CH), 2.86 (m, 1 H, ^iPr CH), 2.80 – 2.70 (m, 2 H, ^iPr CH), 2.66 (d, J = 5.8 Hz, 1 H, CH-Ph), 1.59 (s, 3 H, CH₃), 1.57 (d, J = 6.7 Hz, 3 H, ^iPr CH₃), 1.43 (d, J = 6.7 Hz, 6 H, ^iPr CH₃), 1.39 (d, J = 6.7 Hz, 3 H, ^iPr CH₃), 1.32 (d, J = 6.7 Hz, 3 H, ^iPr CH₃), 1.31 (d, J = 6.7 Hz, 3 H, ^iPr CH₃), 1.29 (d, J = 6.7 Hz, 3 H, ^iPr CH₃), 1.21 – 1.15 (m, 12 H, ^iPr CH₃), 1.03 – 0.97 (m, 9 H, ^iPr CH₃), 0.78 (d, J = 6.7 Hz, 3 H, ^iPr CH₃), 0.72 (d, J = 6.7 Hz, 3 H, ^iPr CH₃), 0.57 (d, J = 6.7 Hz, 3 H, ^iPr CH₃). ^{13}C NMR (151 MHz, C_6D_6) δ 155.67, 153.48, 150.41, 149.87, 146.41, 136.36, 135.74, 130.22, 129.93, 128.82, 127.88, 127.14, 125.85, 125.37, 122.70 (br), 121.30, 122.40, 121.36, 122.42, 119.56, 71.61, 58.17, 38.23, 35.73, 35.12, 35.12, 34.58 (br), 33.22, 28.67, 27.13, 26.27, 26.11, 25.48, 25.46, 24.07 (br), 22.89, 22.82, 21.71, 21.50, 13.60. ^{29}Si - ^1H gHMBC NMR (C_6D_6 , 119 MHz): δ = -14 (SiTip₂), -16 (SiPhTip). ESI-MS m/z 951.6296 (calcd for $\text{C}_{64}\text{H}_{88}\text{NaOSi}_2$, 951.6271).

2.5 References

1. Ottosson, H.; Steel, P. G.; *Chem. Eur. J.*, **2006**, *12*, 1576.
2. Bejan, I.; Scheschkewitz, D.; *Angew. Chem. Int. Ed.*, **2007**, *46*, 5783.
3. Majumdar, M.; Bejan, I.; Huch, V.; White, A. J. P.; Whittell, G. R.; Schafer, A.; Manners, I.; Scheschkewitz, D.; *Chem. Eur. J.*, **2014**, *20*, 9225.
4. Meltzer, A.; Majumdar, M.; White, A. J. P.; Huch, V.; Scheschkewitz, D.; *Organometallics*, **2013**, *32*, 6844.
5. Fink, M. J.; DeYoung, D. J.; West, R. J.; *J. Am. Chem. Soc.*, **1983**, *105*, 1070.
6. Leszcynska, K.; Abersfelder, K.; Mix, A.; Neumann, B.; Stammler, H. G.; Cowley, M. J.; Jutzi, P.; Scheschkewitz, D.; *Angew. Chem. Int. Ed.*, **2012**, *51*, 6785.
7. Gottschling, S. E.; Milnes, K. K.; Jennings, M. C.; Baines, K. M.; *Organometallics*, **2005**, *24*, 3811.
8. Milnes, K. K.; Gottschling, S. E.; Baines, K. M.; *Org. Biomol. Chem.*, **2004**, *2*, 3530.
9. Gottschling, S. E.; Jennings, M. C.; Baines, K. M.; *Can. J. Chem.*, **2005**, *83*, 1568.
10. Milnes, K. K.; Jennings, M. C.; Baines, K. M.; *J. Am. Chem. Soc.*, **2006**, *128*, 2491.
11. Laub, H. A.; Evano, G.; Mayr, H.; *Angew. Chem. Int. Ed.*, **2014**, *53*, 4968.
12. Levens, A.; An, F.; Breugst, M.; Mayr, H.; Lupton, D. W.; *Org. Lett.*, **2016**, *18*, 3566.

Mayr, H.; Lakhdar, S.; Maji, B.; Ofial, A. R.; Beilstein *J. Org. Chem.*, **2012**, 8, 1458.

13. Pavelka, L. C.; Baines, K. M.; *Organometallics*, **2011**, 30, 2261.

14. Tashkandi, N. Y.; Pavelka, L. C.; Hanson, M. A.; Baines, K. M.; *Can. J. Chem.*, **2014**, 92, 462.

15. Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*; 4th Ed.; Oxford; Boston: Butterworth Heinemann, 1996.

16. Bruker-AXS, SAINT version 2013.8, **2013**, Bruker-AXS, Madison, WI 53711, USA

17. Bruker-AXS, SADABS version 2012.1, **2012**, Bruker-AXS, Madison, WI 53711, USA

18. Sheldrick, G. M., *Acta Cryst.* **2015**, A71, 3-8

19. Sheldrick, G. M., *Acta Cryst.* **2015**, C71, 3-8

20. Bruker-AXS, XP version 2013.1, **2013**, Bruker-AXS, Madison, WI 53711, USA

Chapter 3

3 Investigation into the Mechanism of the Addition of Alkynes to an NHC-Stabilized Silylene

3.1 Introduction

Silylenes, the silicon analogue of carbenes, are an important class of compounds which are utilized as ligands for transition metal complexes,¹ in the activation of small molecules,² and as building blocks for many silicon-containing heterocycles.³ With both an empty *p*-orbital and a lone pair, silylenes are ground state singlets and ambiphilic: they can act as either nucleophiles or electrophiles. The cycloaddition of alkynes to silylenes has been extensively studied.⁴ While transient silylenes produce numerous products upon the addition of an alkyne, stable silylenes with bulky or electronically-stabilizing substituents, react with alkynes to afford silacyclopropenes.⁵ Through DFT studies, the silylene was determined to act, in general, as an electrophile.⁶ However, the coordination of Lewis bases to silylenes (Chart 3.1) has been shown to reduce the electrophilic character of silylenes and to alter their reactivity.⁷ With the recent increase in the interest in Lewis base-stabilized silylenes, it is important to understand their reactivity. In this work, a brief history of the development of the chemistry of base-stabilized silylenes will be discussed with a focus on N-heterocyclic carbene-stabilized silylenes and their reactions with alkynes.

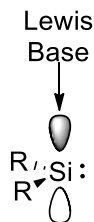
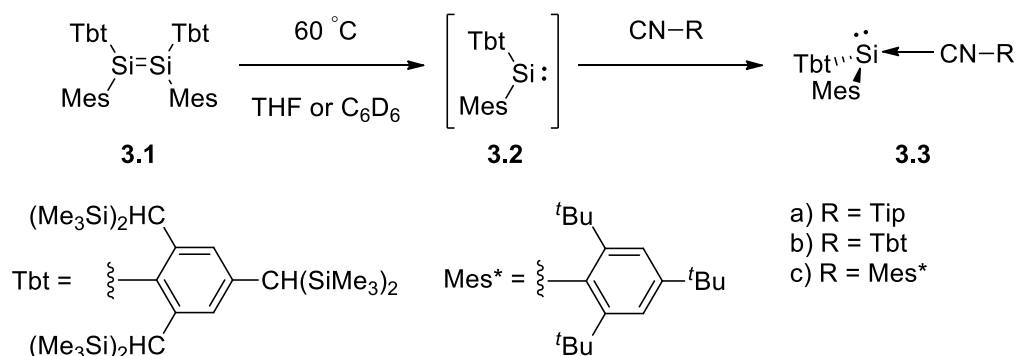


Chart 3.1: Representation of a Lewis-base stabilized silylene.

While the chemistry of base-stabilized silylenes dates to the late 1980's,⁸ the first base-stabilized silylenes were quite reactive and were only observed directly at low temperatures or indirectly through trapping reactions.⁹ The first stable base-stabilized silylene was reported by Okazaki and coworkers (Scheme 3.1).¹⁰

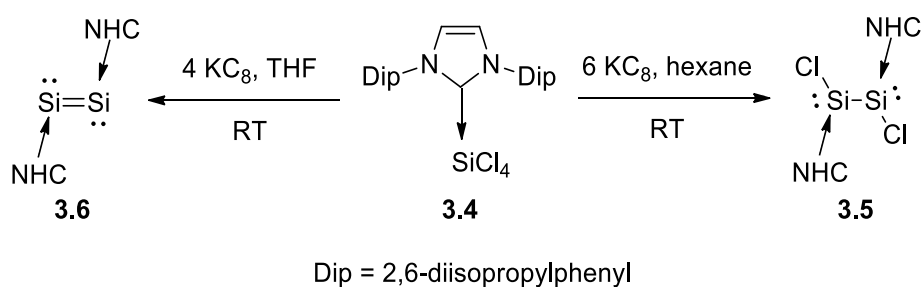


Scheme 3.1: Synthesis of stable Lewis base-stabilized silylenes **3.3**.

Disilene **3.1**, which features bulky aromatic substituents, easily dissociates at mild temperatures to give the transient silylene **3.2**. Heating disilene **3.1** in the presence of an aryl isocyanide led to the formation of complexes **3.3a-c**. While silylene **3.2** was not

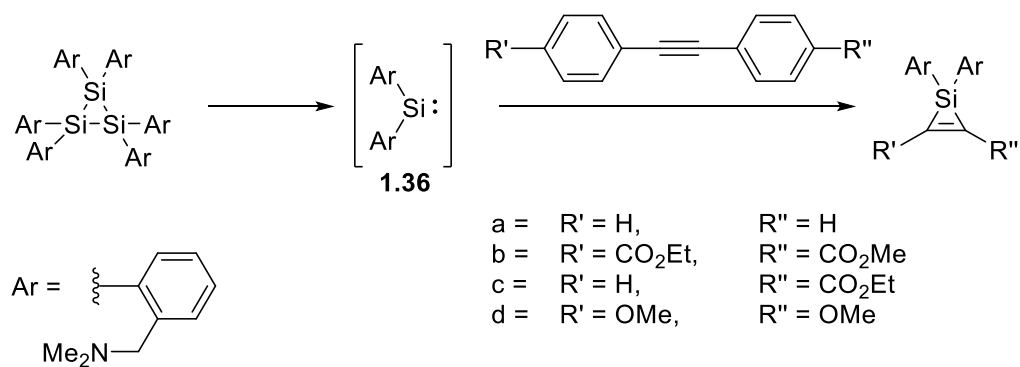
observed directly, the Lewis base-stabilized silylene **3.3a-c**, although air- and moisture-sensitive, are stable in solution for several hours at 60 °C.

The first example of an NHC-stabilized silylene was reported in 2008 by Robinson and co-workers.¹¹ The reduction of the neutral hypercoordinate silicon-carbene complex **3.4** with potassium graphite yielded the NHC-stabilized bis(silylene) **3.5** as well as the NHC-stabilized disilicon fragment **3.6** (Scheme 3.2).



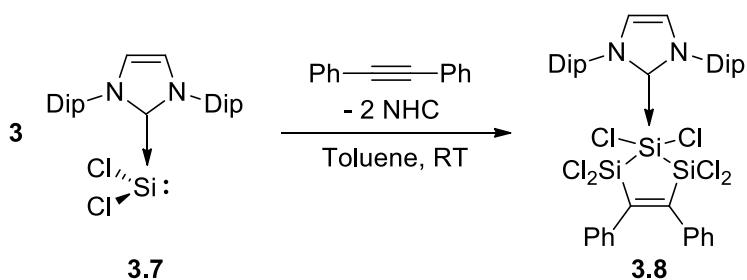
Scheme 3.2: Synthesis of the first NHC-stabilized silylenes **3.5** and **3.6**.

A mechanistic study by Belzner illustrates the effect of a Lewis base on the reactivity of silylenes. The reactivity of the bis(aryl) silylene **1.36** with a variety of acetylenes was examined (Scheme 3.3).¹² A Hammett study provided insight into the philicity of the silylene **1.36**. The positive reaction constant ($\rho = +0.85 \pm 0.21$) was comparable to the reaction of cycloheptatrienyliene, a nucleophilic carbene, and styrene. Normally, stable silylenes act as electrophiles in the cycloaddition with alkynes. The nucleophilic character of silylene **1.36** is attributed to coordination of the NMe₂ groups on the Ar substituents with the silicon centre reducing the electrophilicity of the silylene.



Scheme 3.3: Generation of transient silylene **1.36** and subsequent addition of various acetylenes.

The reactivity of NHC-stabilized silylenes with alkynes was not examined until this past decade. Roesky and Stalke examined the addition of an alkyne to the NHC-stabilized dichlorosilylene **3.7** in 2009.¹³ Complex **3.7** was reacted with diphenylacetylene which afforded the 1,2,3-trisilacyclopent-4-ene **3.8** (Scheme 3.4).

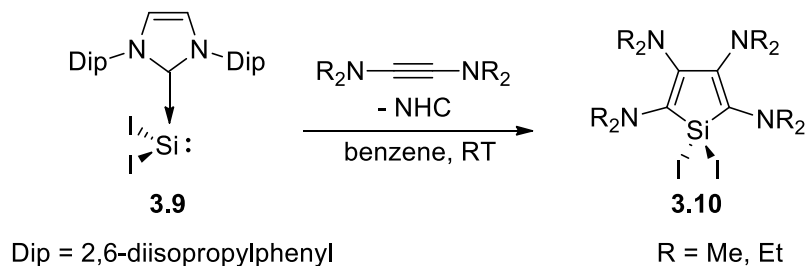


Dip = 2,6-diisopropylphenyl

Scheme 3.4: Addition of diphenylacetylene to NHC-stabilized silylene **3.7**.

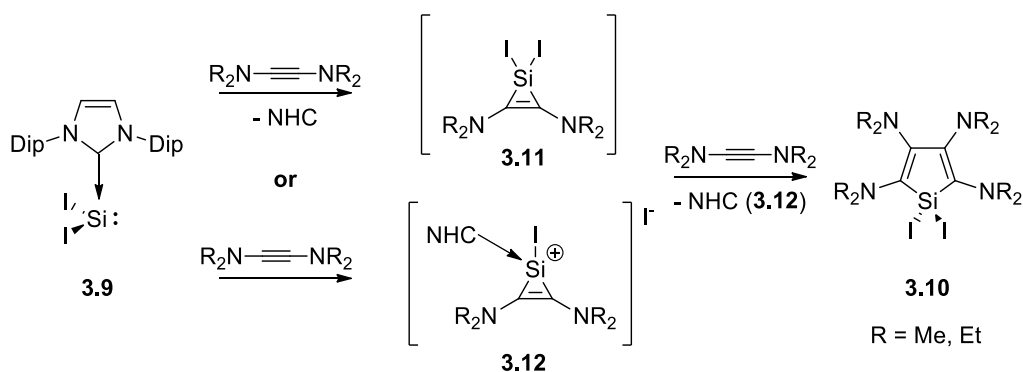
Filippou reported the synthesis of the NHC-stabilized silylene **3.9** which features two iodide substituents on silicon.¹⁴ The addition of bis(dimethylamino)acetylene or

bis(diethylamino)acetylene to silylene **3.9** resulted in the formation of silole **3.10** (Scheme 3.5).



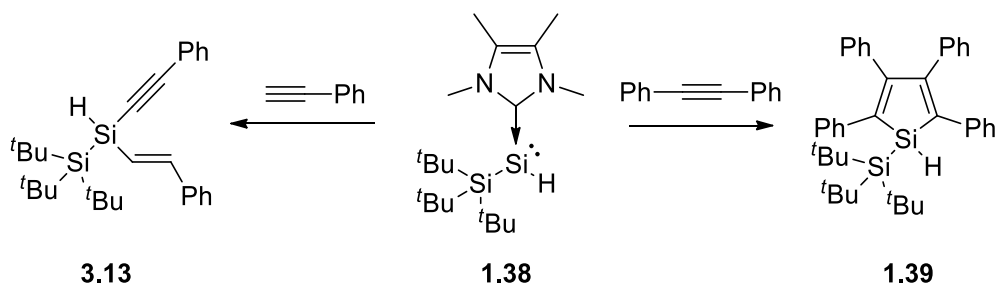
Scheme 3.5: The reaction between bis(amino)acetylenes and silylene **3.9**.

Filippou proposed two possible pathways for the formation of **3.10** (Scheme 3.6): the first involves the substitution of the NHC by the ynediamine to give silacyclopropene **3.11** and the second involves substitution of an iodide by a ynediamine to give the silacyclopropenium intermediate **3.12**. While these are plausible mechanisms, there was no experimental or computational evidence to support either proposal.



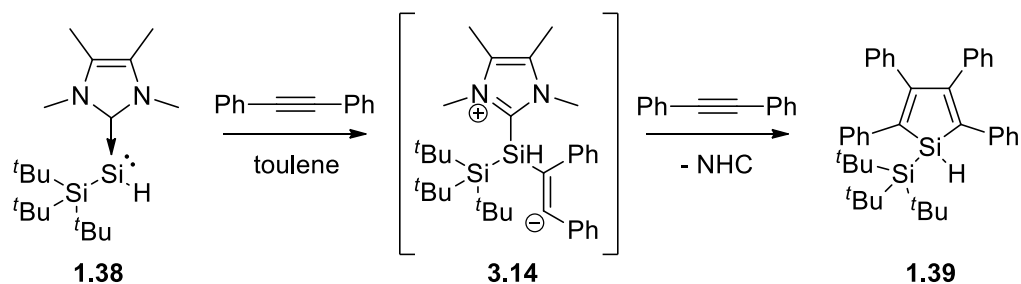
Scheme 3.6: Proposed mechanisms for the formation of **3.10**.

The formation of a silole in the reaction between a silylene and an alkyne was also observed by Inoue.¹⁵ The NHC-stabilized silylene **1.38** was reacted with both phenylacetylene and diphenylacetylene. In the latter case, silole **1.39** was isolated. When silylene **1.38** was reacted with the terminal alkyne, the formation of a silole was not observed; compound **3.13** was isolated from the reaction.



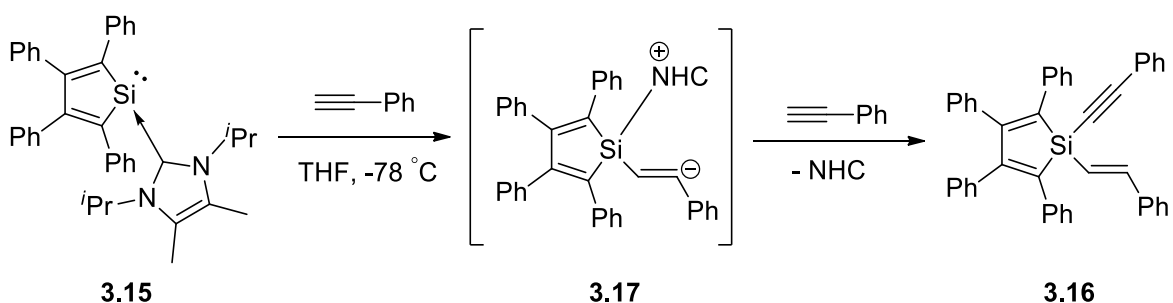
Scheme 3.7: Reaction of phenylacetylene and diphenylacetylene with silylene **1.38**.

The mechanism of formation of silole **1.39** was studied using DFT calculations. The energetics of three distinct pathways were calculated: the formation of a silacyclopropene and the formation of a silacyclopropenium intermediate, both of which were described previously by Filippou, and a third pathway where silylene **1.38** undergoes nucleophilic addition to the alkyne, forming the ionic intermediate **3.14**. Nucleophilic addition of the zwitterion to another equivalent of alkyne followed by ring closure and loss of the NHC gives silole **1.39**. The latter was determined to be the lowest energy pathway for the formation of **1.39** (Scheme 3.8).



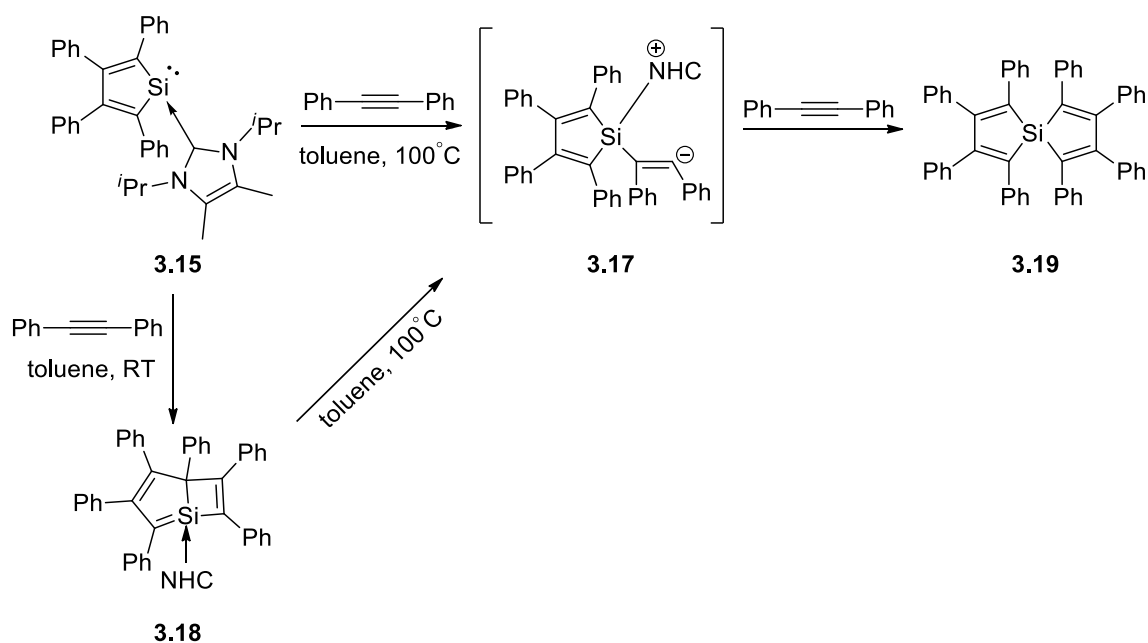
Scheme 3.8: The favoured pathway to silole **1.39**.

Cui *et al.* reported the synthesis of silylene **3.15**, an NHC-stabilized silacyclopentadienylidene.¹⁶ Upon addition of two equivalents of phenylacetylene, the formation of the 1-alkenyl-1-alkynylsilole **3.16** was observed (Scheme 3.9). The reaction is proposed to proceed through the zwitterion **3.17**, which subsequently abstracts a hydrogen from another equivalent of the terminal alkyne, followed by substitution of the NHC by the alkynyl anion yielding **3.16**.



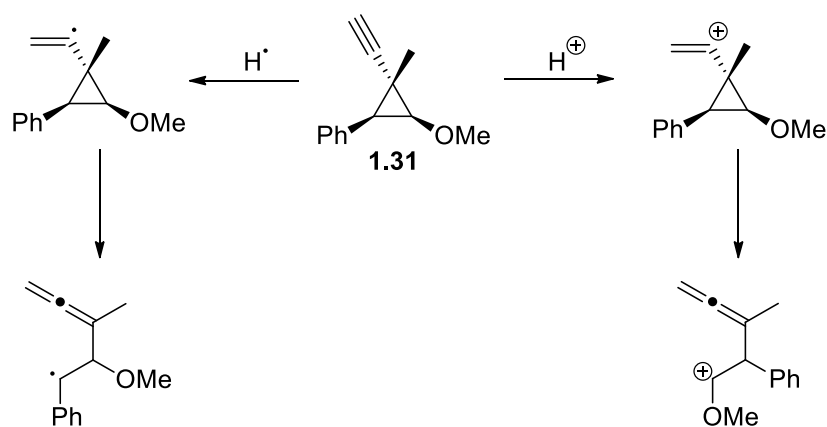
Scheme 3.9: Addition of phenylacetylene to silylene **3.15** and the proposed zwitterionic intermediate.

Cui *et al.* recently revisited the addition of alkynes to silylene **3.15**;¹⁷ the addition of internal alkynes to **3.15** was examined. The addition of one equivalent of diphenylacetylene to **3.15** yielded the 1:1 adduct **3.18** as a dark green solid (Scheme 3.10). Compound **3.18** slowly decomposes in solution and could not be characterized by X-ray crystallography. The formation of a second compound, a 1:2 silylene:acetylene adduct, was also observed by NMR spectroscopy. Reaction of silylene **3.15** with 2 equivalents of diphenylacetylene at 100 °C, or the reaction of **3.18** with 1 equivalent of diphenylacetylene at 100 °C, led to the formation of the spirocyclic bis(silole) **3.19**. The proposed intermediate was analogous in structure to the zwitterionic intermediate **3.14** as reported by Inoue.



Scheme 3.10: Addition of an internal alkyne to silylene **3.15**.

While the mechanism of the addition of alkynes to NHC-stabilized silylenes has been studied using computational methods, there have been no experimental studies. The Baines group has studied the mechanism of the cycloaddition of alkynes to disilenes, the dimer of silylenes, utilizing a mechanistic probe, alkyne **1.31**.¹⁸ **1.31** features a phenyl and methoxy substituent on the cyclopropyl ring. If a vinyl cation is present α to the cyclopropyl ring, then the ring regioselectively opens towards the methoxy substituent. However, if a radical is α to the cyclopropyl ring, then the ring regioselectively opens towards the phenyl substituent (Scheme 3.11).¹⁹ These ring opening processes have a rate constant of $10^{10} - 10^{12} \text{ s}^{-1}$ which is greater than other competitive processes. If an anion is generated adjacent to the cyclopropyl ring (as modelled by the vinyl lithium derivative), the ring does not open. The regiochemistry of the phenyl and methoxy substituents in the products of the reaction reveal the nature of the intermediate during the reaction.



Scheme 3.11: The regioselectivity of cyclopropyl ring opening.

In this study, the addition of alkyne **1.31** to the NHC-stabilized silylene **1.38**, synthesized by Inoue, was examined to determine the nature of the intermediate formed when **1.38** reacts with alkynes.

3.2 Results and Discussion

Cyclopropyl alkyne **1.31** was added to an equimolar red solution of silylene **1.38** in toluene at room temperature and left to stir overnight. The colour of the solution deepened to dark red within a few minutes of addition. The solvent was removed to yield a dark red oil. A precipitate was removed by washing with hexanes. The residue from the mother liquor was separated by preparative thin-layer chromatography. Compound **3.20** was isolated and characterized by ^1H , ^{13}C , ^1H - ^1H gCOSY, ^{13}C - ^1H gHSQC, ^{13}C - ^1H gHMBC and ^{29}Si - ^1H gHMBC NMR spectroscopy as well as ESI-mass spectrometry.

3.2.1 Structure Elucidation

The ^1H NMR spectrum of **3.20** is shown in Figure 3.1. Two isomers are evident in a ratio of approximately 2:1 (Figure 3.1e). The ESI mass spectrum of **3.20** revealed a signal at m/z 665.4 which corresponds to a 2:1 adduct of silylene **1.38** and alkyne **1.31** (plus a sodium ion).

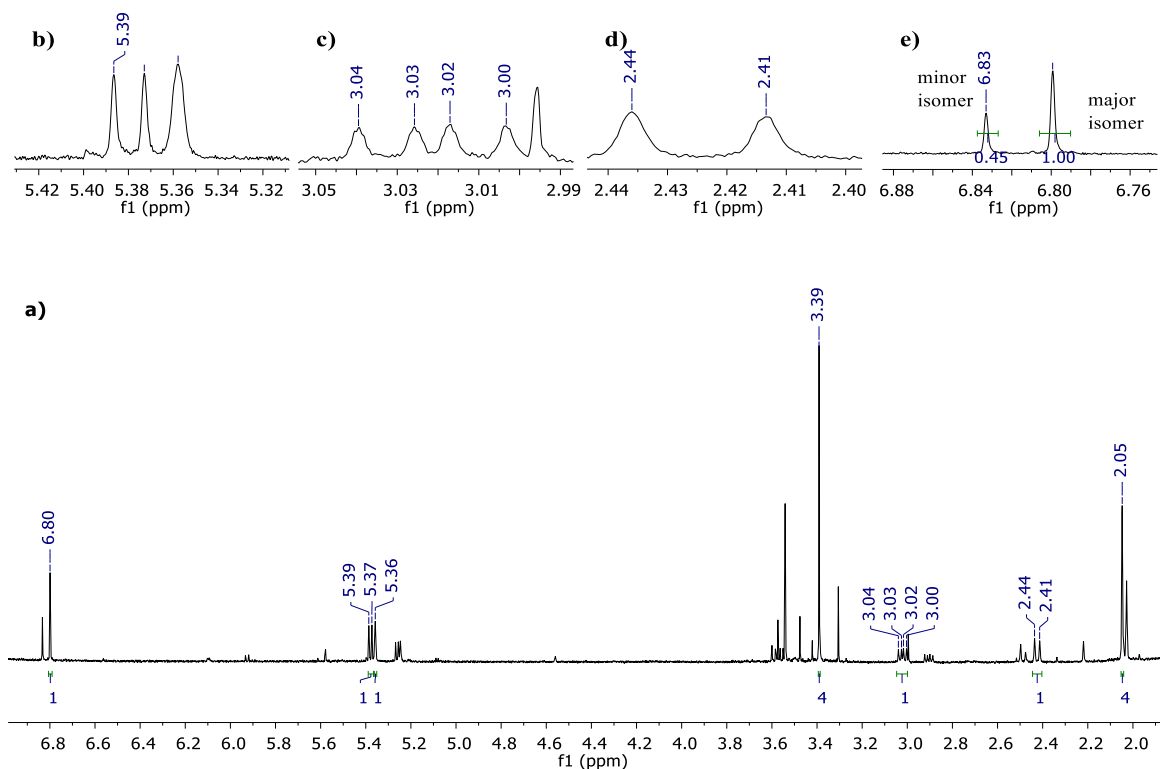


Figure 3.1: ^1H NMR spectrum of **3.20** (C_6D_6 , 600 MHz). Expansions from a) 1.9-6.9 ppm b) 5.31-5.43 ppm c) 2.98-3.06 ppm d) 2.39-2.45 ppm e) 6.75-6.89 ppm.

The two equivalents of silylene was consistent with the number of signals observed in the ^{29}Si - ^1H gHMBC spectrum of **3.20**; four signals were observed. Two of the four signals, at 5 ppm and 16 ppm, correlated to signals in the ^1H dimension at 1.29 ppm and 1.17 ppm, respectively. On the basis of the chemical shift and the integration of the ^1H signals (27 H), the signals at 5 and 16 ppm in the ^{29}Si dimension were assigned to Si^tBu_3 groups. In addition, the signal at 5 ppm in the ^{29}Si dimension correlated to a doublet at 5.38 ppm in the ^1H dimension, while the signal at 16 ppm in the ^{29}Si dimension correlated to a singlet at 5.36 ppm in the ^1H dimension.

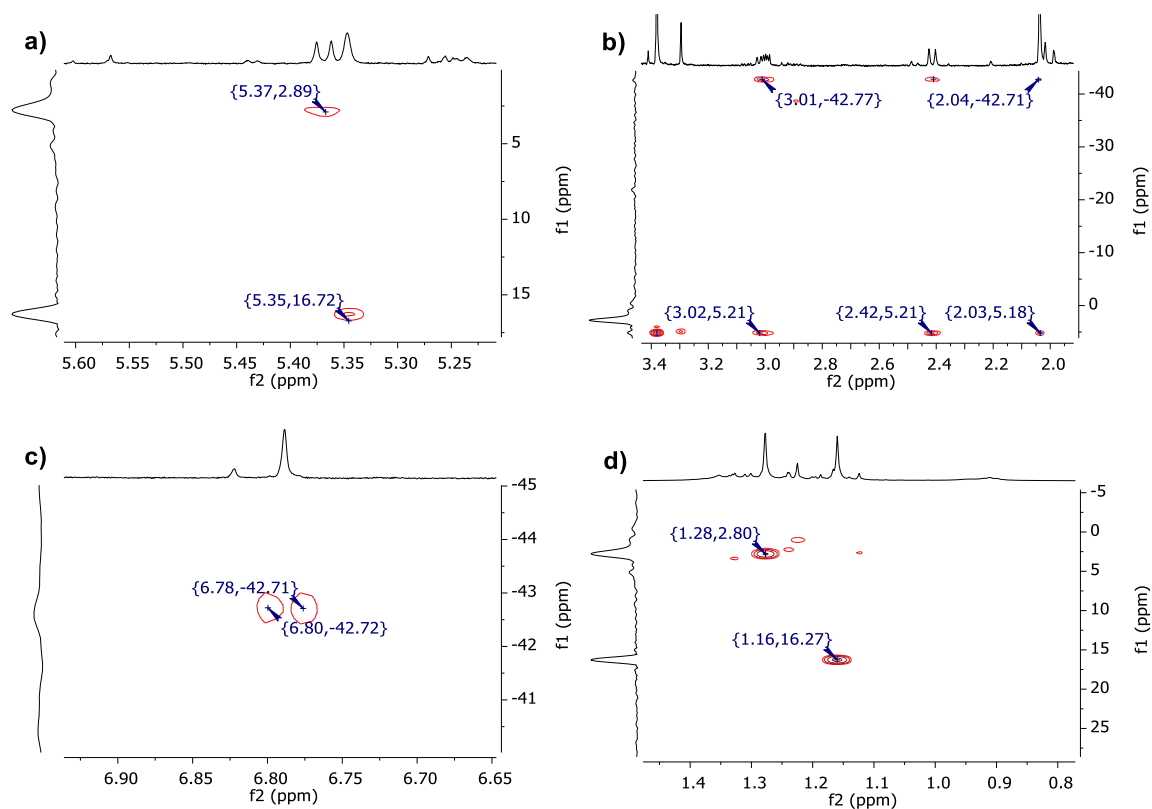


Figure 3.2: Expansion of the ^{29}Si - ^1H gHMBC NMR spectrum of **3.20** (600 MHz, C_6D_6) with ^1H ranges of: a) 5.25-5.60 ppm; b) 2.00-3.40 ppm; c) 6.65-6.90 ppm; d) 0.8-1.4 ppm.

The ^1H signals at 5.38 ppm and 5.36 ppm integrate to one hydrogen and show no correlations in the ^{13}C - ^1H gHSQC spectrum of **3.20**, and thus, the ^1H signals were assigned to silicon hydrides. The doublet at 5.38 ppm in the ^1H dimension correlates in the ^1H - ^1H gCOSY spectrum of **3.20** to a doublet of doublets at 3.02 ppm. The signal at 3.02 ppm also correlates to a doublet at 2.43 ppm in the ^1H - ^1H gCOSY spectrum (Chart 3.2). A correlation was observed in the ^{13}C - ^1H gHSQC spectrum of **3.20** between the signals at 3.02 ppm and 2.43 ppm in the ^1H dimension, and a signal at 25.8 ppm in the ^{13}C dimension. Since both the ^1H signals at 3.02 and 2.43 ppm correlate to the same

carbon signal, and integrate to 1H each, the signals at 3.02 and 2.43 ppm were assigned to a **CH₂** group. The unassigned ²⁹Si signals, at -43 and 3 ppm in the ²⁹Si-¹H gHMBC spectrum of **3.20**, correlate to the signals at 3.02 ppm and 2.43 ppm in the ¹H dimension. On the basis of these data, the structure of the fragment shown in Chart 3.2 was deduced.

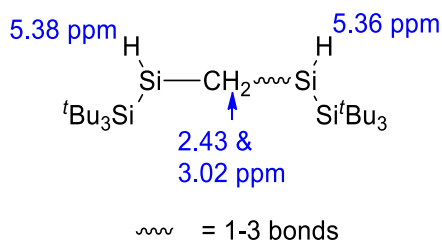


Chart 3.2: Fragment of **3.20** based on correlations in the ²⁹Si-¹H gHMBC and ¹H-¹H gCOSY NMR spectra.

The ¹³C-¹H gHMBC spectrum of **3.20** revealed that several signals in the ¹H dimension, including the signals assigned to the CH₂ group, correlated to a small subset of signals in the ¹³C dimension (Figure 3.3). These correlations are outlined in Table 3.1.

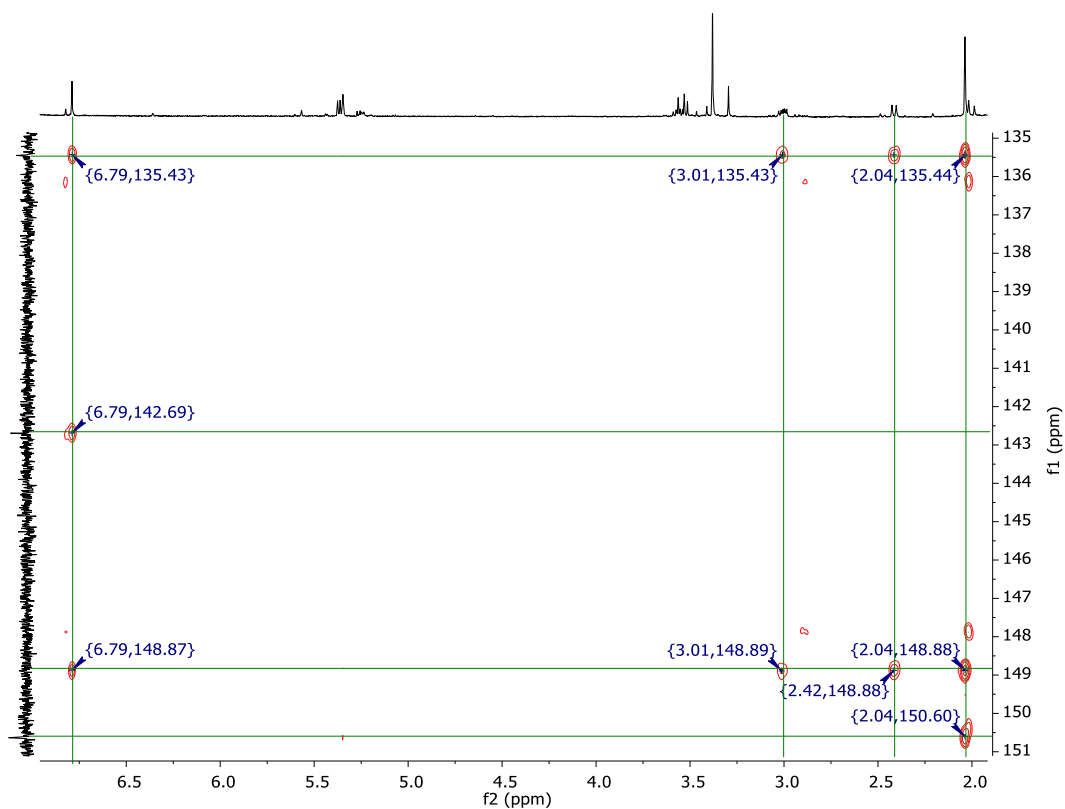


Figure 3.3: Expansion of the ^{13}C - ^1H gHMBC NMR spectrum of **3.20** between 2.0-7.0 ppm in the ^1H dimension and 135.0-151.0 in the ^{13}C dimension (600 MHz, C_6D_6).

Table 3.1: ^{13}C - ^1H HMBC correlations utilized in elucidating the core structure of **3.20**.

Multiplicity & Integration	^1H NMR Chemical Shift	Correlations evident in the ^{13}C - ^1H HMBC spectrum
s, 1H	6.80 ppm	135.44 ppm, 142.69 ppm, 148.88 ppm
dd, 1H	3.02 ppm	135.44 ppm, 148.88 ppm
d, 1H	2.43 ppm	135.44 ppm, 148.88 ppm
s, 3H	2.05 ppm	135.44 ppm, 148.88 ppm, 150.60 ppm

The ^1H NMR signals at 6.80 ppm and 2.05 ppm correlated to signals in the ^{13}C dimension of the ^{13}C - ^1H gHSQC spectrum of **3.20** at 150.60 ppm and 17.48 ppm, respectively. On the basis of the chemical shifts and the correlations, the signal at 6.80 ppm in the ^1H NMR spectrum was assigned to a C=CH- group, while the signal at 2.05 ppm was assigned as a methyl group. The ^{13}C chemical shifts of the signals listed in Table 3.1 are sp^2 -hybridized carbons on the basis of their chemical shifts. The alkenyl hydrogen, at 6.80 ppm in the ^1H dimension correlated to the ^{29}Si signal at -43 ppm in the ^{29}Si - ^1H gHMBC spectrum of **3.20**. On the basis of this correlation and the chemical shift of the ^{29}Si signal, the signal at -43 ppm in the ^{29}Si dimension was assigned to a silole silicon. From the ^{29}Si and ^{13}C chemical shifts, as well as correlations in the ^{13}C - ^1H gHMBC NMR spectrum of **3.20**, the silole fragment, illustrated in Chart 3.3, was elucidated.

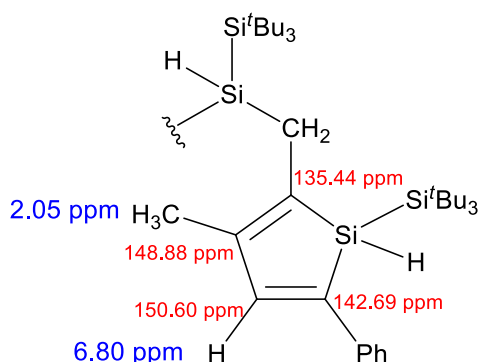
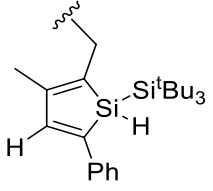
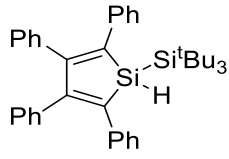


Chart 3.3: Fragment of **3.20** with silole ring ^1H and ^{13}C chemical shifts listed.

A comparison of the ^1H , ^{13}C , and ^{29}Si chemical shifts for **3.20** and **1.39** (Table 3.2) reveals that the ^1H chemical shifts assigned to the Si-H differ only by 0.33 ppm, and the chemical shifts of the ^{29}Si signals in the silole rings differ only by 7.8 ppm. The ^{13}C signals in **3.20** were assigned on the analysis of ^{13}C - ^1H HMBC NMR spectrum of **3.20**.

The trend in chemical shifts is similar to that observed for **1.39**. The signals at higher field were assigned to the carbons adjacent to the silicon in the silole ring and the signals at lower field were assigned to the carbons β to the silicon.

Table 3.2: ^1H , ^{13}C , and ^{29}Si chemical shifts for **3.20** and **1.39**.

	 3.20	 1.39
^1H Chemical Shifts		
Si-<u>H</u>	5.36 ppm	5.69 ppm
^{13}C Chemical Shifts		
α to Si	142.69 ppm (<u>C</u> -Ph)	143.3 ppm (<u>C</u> -Ph)
	135.56 ppm (<u>C</u> -CH ₂)	
β to Si	150.60 ppm (<u>C</u> -H)	157.6 ppm (<u>C</u> -Ph)
	148.80 ppm (<u>C</u> -CH ₃)	
^{29}Si Chemical Shifts		
Silole <u>Si</u>	-43 ppm	-34.2 ppm
<u>Si</u> ^t Bu ₃	16 ppm	18.3 ppm

One substituent remains unidentified in the fragment as shown in Chart 3.3. A singlet, with an integration of three, was observed at 3.39 ppm in the ^1H NMR spectrum of **3.20**.

This signal correlates to the signal at 56.10 ppm in the ^{13}C dimension of the ^{13}C - ^1H

gHSQC NMR spectrum of **3.20**, and the signal at 3 ppm in the ^{29}Si dimension of the ^{29}Si - ^1H gHMBC NMR spectrum of **3.20**. On the basis of the ^1H and ^{13}C chemical shifts and the integration, these signals were assigned to a methoxy group. The only correlation to either the ^1H signal at 3.39 ppm or the ^{13}C signal at 56.10 ppm in the ^{13}C - ^1H gHMBC NMR spectrum, was between the signal at 56.10 ppm in ^{13}C dimension and the signal at 5.38 ppm in the ^1H dimension, which was assigned to the silicon hydride. Thus, the methoxy group is bound to the silicon with a chemical shift of 3 ppm. The final elucidated structure is shown in Chart 3.4.

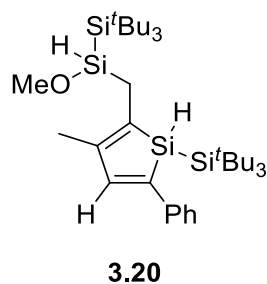
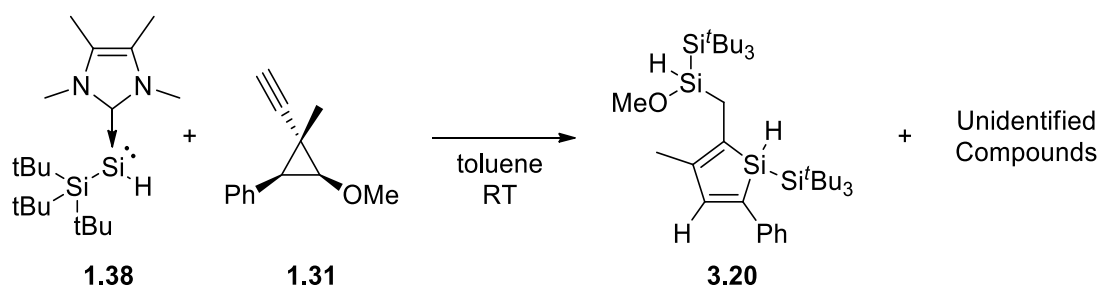


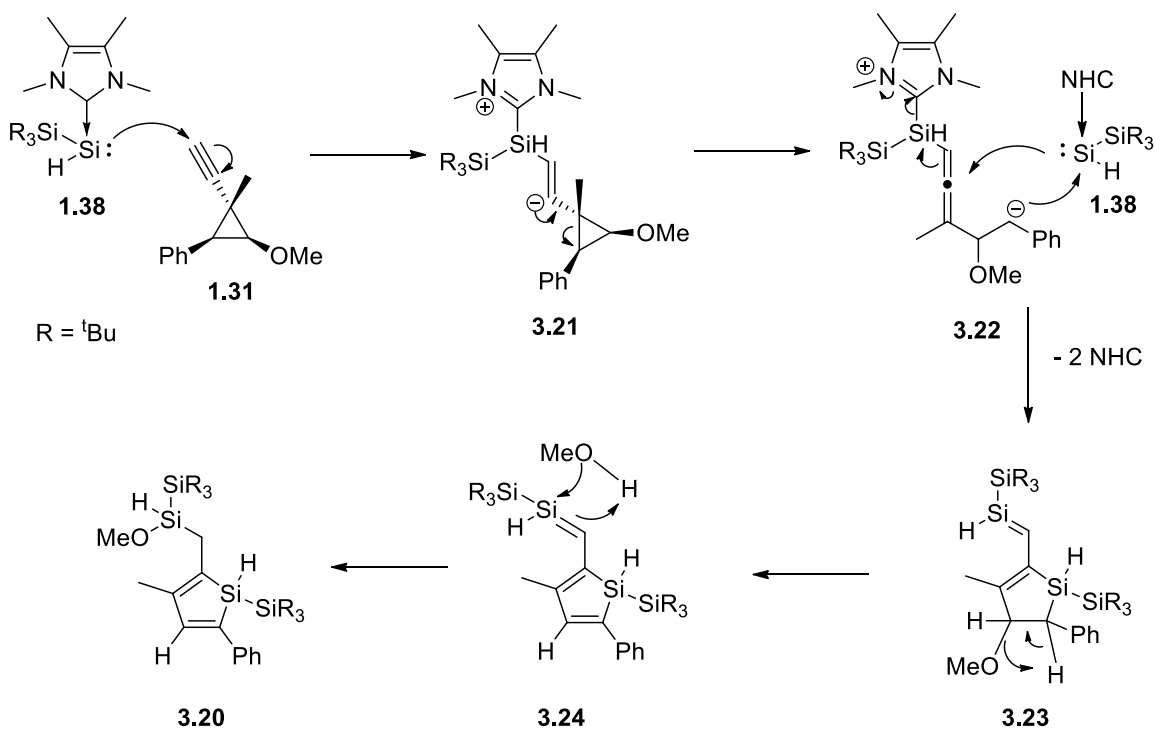
Chart 3.4: The final elucidated structure for **3.20**.

3.2.2 Mechanistic Insights



Scheme 3.12: The reaction of silylene **1.38** with alkyne **1.31**.

3.20 was isolated in a yield of 2 %. While this yield is low, a mass loss of 83% was observed after the plate and **3.20** made up 10 % of the material recovered from the plate. A proposed reaction mechanism for the formation of **3.20** is presented in Scheme 3.13.



Scheme 3.13: The proposed mechanism for the formation of **3.20**.

Nucleophilic addition of silylene **1.38** to alkyne **1.31** leads to the formation of zwitterion **3.21**. Regioselective ring opening of the cyclopropane towards the phenyl substituent leads to **3.22** which reacts with another equivalent of silylene **1.38** to form intermediate **3.23** accompanied by the loss of two equivalents of NHC. Although the formation of **3.23** is shown as a concerted process, a multi-step transformation is

possible. Loss of methanol from **3.23** would give the silole-substituted silene, **3.24**. Subsequent addition of methanol to the silene moiety of **3.24** results in the formation of **3.20**.

The addition of alkyne **1.31** to silylene **1.38** can reasonably proceed through two pathways: with the silylene acting as the nucleophile or with the silylene acting as the electrophile. If the reaction proceeds with **1.38** acting as an electrophile, then the cyclopropyl ring of alkyne **1.31** would be expected to open towards the methoxy substituent as has been demonstrated previously.^{19,20} However, the regiochemistry of the phenyl substituent in the final product, **3.20**, suggests this is not case. The formation of **3.20** is most reasonably explained by silylene **1.38** acting as a nucleophile in the first step, generating an α -anion, and regioselective opening of the cyclopropyl ring towards the phenyl substituent. The structure of the first intermediate formed, **3.21**, is analogous to those proposed by Inoue and Cui (Chart 3.5) and provides supporting evidence that the silylene is the nucleophile in the reaction with alkynes.

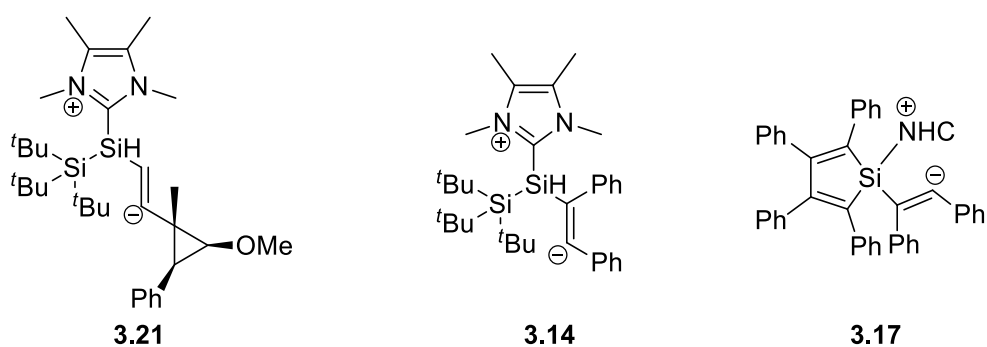
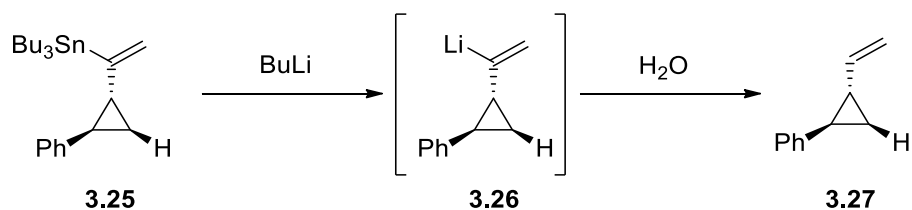


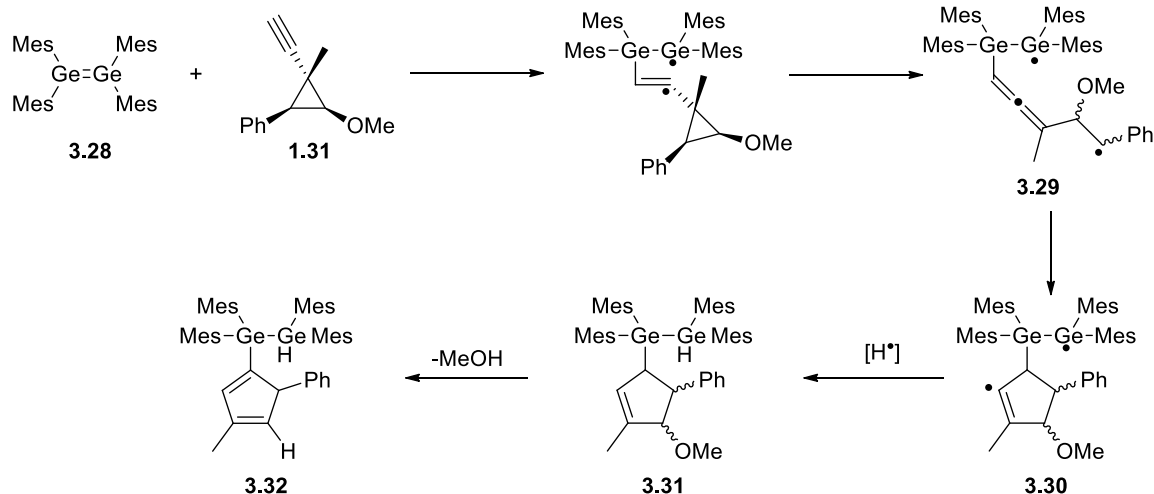
Chart 3.5: Comparison of the structure of **3.21** with the analogous zwitterionic intermediates proposed by Inoue and Cui.

The behaviour of **3.21** with a negative charge of a zwitterion on the vinylic carbon adjacent to the cyclopropyl ring contrasts with the behaviour of vinyl lithium **3.26** which did not undergo ring opening (Scheme 3.14). The difference in reactivity is attributed to having a full charge with a covalently bound Li in contrast to a negative charge in a zwitterion.



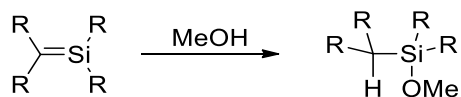
Scheme 3.14: Reaction of **3.25** with butyllithium.

The formation of silole **3.20** is reminiscent of the formation of a cyclopentadiene that was observed in the reaction of tetramesityldigermene **3.28** and cyclopropyl alkyne **1.31** (Scheme 3.15). In addition to undergoing ring closure to give a 7-membered allene compound (not shown), the biradical **3.29** undergoes ring closure to give **3.30** which, after hydrogen abstraction gives **3.31**. Loss of methanol gives **3.32**.



Scheme 3.15: Mechanism for the addition of cyclopropyl probe **1.31** to tetramesityldigermene **3.28**.

Interestingly, the loss of methanol proposed during the formation of **3.20** was also proposed in the formation of **3.32** (Scheme 3.15). The regioselective addition of methanol to the silenic moiety of **3.24** gives **3.20**. The regioselective addition of methanol to silenes to give methoxysilanes is a well-known reaction in silene chemistry (Scheme 3.16).²¹



Scheme 3.16: Addition of methanol to a silene.

3.3 Conclusions

To summarize, the reaction between NHC-stabilized silylene **1.38** and alkyne **1.31** was studied. **3.20** was isolated from the crude mixture and a mechanism for the formation was proposed. The most reasonable pathway to silole **3.20** includes silylene **1.38** acting as a nucleophile. The reaction pathway proposed is consistent with previous studies of the reaction of alkynes with base-stabilized silylenes.¹² Combining all studies to date, there is increasing evidence that base-stabilized silylenes act as nucleophiles, particularly in the reaction with alkynes.

The results of this study provide important implications for understanding the chemistry of probe **1.31**. Early studies demonstrated that the cyclopropyl ring of **1.31** opens regioselectively in the presence of an α -cation or α -radical;¹⁸ however, no evidence for ring opening in the presence of α -anion was observed. All experiments where the alkyne **1.31** was used as a mechanistic probe were analyzed under the assumption the cyclopropyl ring would not open if an α -anion was formed. The results herein call into question this assumption and, as such, it is concluded that ring opening of **1.31** towards the phenyl substituent during the course of a reaction can indicate the presence of either a radical or a negative charge from a zwitterion developing on the α -carbon during the reaction.

Interestingly, we observe silylene **1.38** acting as a nucleophile in the reaction with alkyne **1.31** and not as a base. **3.20** only makes up 10% of the products isolated by thin-layer chromatography; other compounds from the plate were not fully characterized. As

such, **3.20** is not completely indicative of the reactivity between silylene **1.38** and alkyne **1.31**. The ^1H NMR spectrum of a compound also isolated by chromatography, showed signals that can be assigned to a phenyl substituent, and thus, is likely derived from alkyne **1.31**. However, due to time constraints, the compound was not isolated cleanly and could not be characterized. Thus, definitive conclusions regarding the reactivity of silylene **1.38** cannot be made at this time.

3.4 Experimental

3.4.1 General Procedure

All reactions were conducted under a nitrogen atmosphere using an MBraun Labmaster 130 glovebox. Pre-coated silica glass plates suitable for preparative thin-layer chromatography were purchased from Millipore Sigma. Solvents and reagents were purified by standard methods.²² Silylene **1.38** was obtained from Dr. S. Inoue, Technische Universität München. Alkyne **1.31** was synthesized by Nada Tashkandi in the Baines lab.

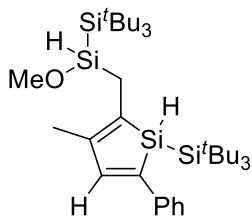
^1H and ^{13}C NMR data were obtained on a 600 MHz INOVA NMR spectrometer. The standards used were as follows: residual $\text{C}_6\text{D}_5\text{H}$ (7.15 ppm) and $(\text{CD}_3)\text{CO}(\text{CD}_2\text{H})$ (2.04 ppm) for ^1H NMR spectra; C_6D_6 (128.00 ppm) and $(\text{CD}_3)_2\text{CO}$ (29.80 ppm) for ^{13}C NMR spectra. J values are reported in Hertz. ESI mass spectra were recorded on a Bruker

microTOF II mass spectrometer with an electrospray interface in positive ion mode (reported in mass-to-charge units, m/z).

3.4.2 Addition of Alkyne **1.31** to Silylene **1.38**

Alkyne **1.31** (26 mg, 0.14 mmol) was added to an orange-red solution of silylene **1.38** (50 mg, 0.14 mmol) dissolved in toluene (~5 mL). The colour of the solution deepened to a dark red. The mixture stirred overnight for 18 h before the solvent was removed under vacuum. The resulting oil was washed with hexanes. The precipitate was separated by centrifugation and the solvent was removed under vacuum. The red residue was dissolved in EtOAc under ambient conditions to give a red solution which quickly faded to light pink. Preparative TLC (100% hexanes, 17% material recovered) was performed and compound **3.20** (in a 2:1 ratio with a second isomer with similar NMR data) was characterized (8 mg, 2 % yield). **3.20** was present as a minor product in the crude product mixture.

Compound **3.20**



Isolated Yield = 2%, $^1\text{H NMR}$ (C_6D_6 , 600 MHz): δ = 7.36 (dd, J = 8.4 Hz, J = 1.4 Hz, 2 H, *o*-Ph-H), 7.19 (masked m, 2 H, *m*-Ph-H), 7.08 (m, 1 H, *p*-Ph-H), 6.80 (s, 1 H, C-CH=C), 5.38 (d, J = 8.2 Hz, 1H, HSi-CH₂), 5.36 (s, 1H, silole SiH), 3.39 (s, 3H, OCH₃), 3.02 (dd, J = 8.2 Hz, J = 13 Hz, 1 H, CH₂), 2.42 (d, J = 13 Hz, 1 H, CH₂), 2.05 (s, 3 H, CH₃),

1.29 (s, 27 H, ^tBu CH₃), 1.17 (s, 27 H, ^tBu CH₃). ¹³C NMR (151 MHz, C₆D₆) δ = 150.70, 144.87, 142.74, 135.49, 129.01, 128.35, 128.22, 128.06, 127.90, 126.35, 56.41, 31.63, 31.61, 31.59, 31.54, 31.45, 25.98, 24.39, 24.33, 23.40, 23.34, 17.75. ²⁹Si-¹H gHMBC NMR (C₆D₆, 119 MHz): δ = 16 (Si'Bu₃), 5 (Si'Bu₃), 3 (Si-CH₂), -43 (Silole Si). ESI-MS: *m/z* 665.4 (calcd for C₃₇H₇₀NaOSi₄, 665.44).

3.5 References

1. a) Benedek, Z.; Szilvási, T.; *RSC Adv.*, **2015**, *5*, 5077; b) Waterman, R.; Hayes, P. G.; Tilley, T. D.; *Acc. Chem. Res.* **2007**, *40*, 712; c) Raoufmoghaddam, S.; Zhou, Y.; Wang, Y.; Driess, M.; *J. Organomet.Chem.*, **2017**, *829*, 2.
2. a) Driess, M.; *Nature*, **2012**, *4*, 525; b) Blom, B.; Driess, M.; *Structure and Bonding (Berlin, Germany)*, **2014**, 156; c) Yao, S.; Xiong, Y.; Driess, M.; *Organometallics*, **2011**, *30*, 1748.
3. a) Ishikawa, M.; *Asian, J. Org. Chem.*, **2015**, *4*, 1192; b) Ghadwal, R. S.; Azhakar, R.; Roesky, H. W.; *Acc. Chem. Res.*, **2013**, *46*, 444.
4. Atwell, W. H.; *Organometallics*, **2009**, *28*, 3573.
5. a) Suzuki, H.; Tokitoh, N.; Okazaki, R.; *Bull. Chem. Soc. Jpn.*, **1995**, *68*, 2471; b) Lips, F.; Mansikkamaki, A.; Fettinger, J. C.; Tuononen, H. M.; Power, P. P.; *Organometallics*, **2014**, *33*, 6253.
6. a) Koch, R.; Bruhn, T.; Weidenbruch, M.; *Organometallics*, **2004**, *23*, 1570; b) Tanaka, H.; Kondo, Y.; Shoitani, Y.; Naka, A.; Ishikawa, M.; Yoshizawa, K.; *Organometallics*, **2011**, *30*, 3160.
7. Belzner, J.; Dehnert, U.; Ihmels, H.; *Tetrahedron*, **2001**, *57*, 511.
8. Belzner, J.; Ihmels, H.; *Adv. Organomet. Chem.*, **1998**, *43*, 1.

9. Gillette, G. R.; Noren, G. H.; West, R.; *Organometallics*, **1989**, *8*, 487.
10. Takeda, N.; Suzuki, H.; Tokitoh, N.; Okazaki, R.; *J. Am. Chem. Soc.* **1997**, *119*, 1456.
11. Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer III, H. F.; Schleyer, P. R.; Robinson, G. H.; *Science*, **2008**, *321*, 1069.
12. Belzner, J.; Dehnert, U.; Ihmels, H.; *Tetrahedron*, **2001**, *57*, 511.
13. Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D.; *Angew. Chem. Int. Ed.*, **2009**, *48*, 5683.
14. Lebedev, Y. N.; Das, U.; Chernov, O.; Schnakenburg, G.; Filippou, A. C.; *Chem. Eur. J.*, **2014**, *20*, 9280.
15. Eisenhut, C.; Szilvási, T.; Breit, N. C.; Inoue, S.; *Chem. Eur. J.*, **2015**, *21*, 1949.
16. Gao, Y.; Zhang, J.; Hu, H.; Cui, C.; *Organometallics*, **2010**, *29*, 3063.
17. Li, T.; Zhang, J.; Cui, C.; *Chem. Asian J.*, **2017**, *12*, 1218.
18. Milnes, K. K.; Pavelka, L. C.; Baines, K. M.; *Chem. Soc. Rev.*, **2016**, *45*, 1019.
19. Gottschling, S. E.; Grant, T. N.; Milnes, K. K.; Jennings, M. C.; Baines, K. M.; *J. Org. Chem.*, **2005**, *70*, 2686.
20. Le Tadic-Biadatti, M.-H.; Newcomb, M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1467.
21. Brook, A. G.; Baines, K. M.; *Adv. Organomet. Chem.* **1986**, *25*, 1.

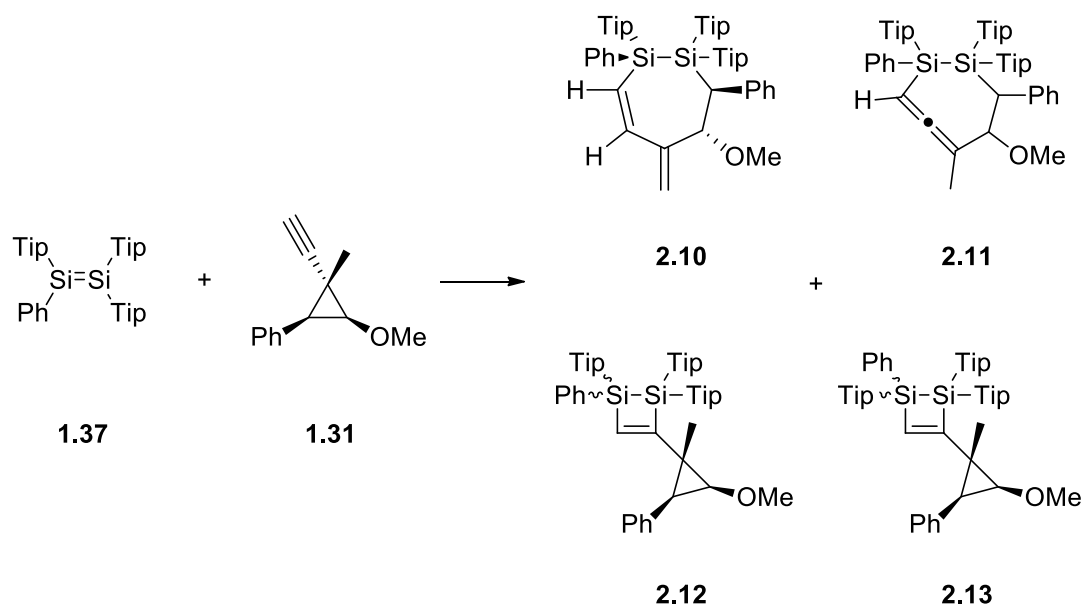
22. Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*; 4th Ed.; Oxford; Boston: Butterworth Heinemann, 1996.

Chapter 4

4 Conclusions and Future Work

4.1 Summary and Conclusions

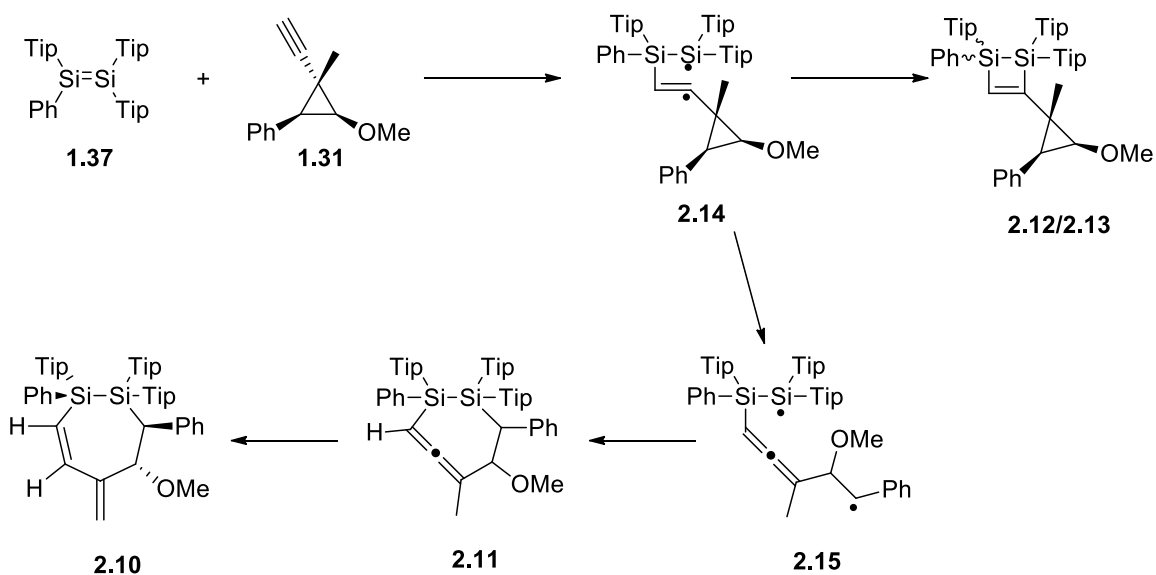
The mechanism of the addition of alkynes to low-valent silicon compounds has been studied using a mechanistic probe approach.¹ When the reactivity of disilene **1.5** with phenylacetylene was reported, the authors stated: “Although the mechanism of the addition reaction of phenylacetylene to **1.5** is unclear, we favor the ionic path in our case because of the polarized nature of the unsymmetrically substituted disilene”.² Likewise, when the reactivity of **1.37** with phenylacetylene was reported, although a biradical mechanism was considered, the authors still hypothesized the formation of a zwitterionic intermediate.³ Using a mechanistic probe approach, the cycloaddition of alkynes to disilenes has been shown to proceed through a stepwise mechanism involving a biradical intermediate.⁴ Until this work, only the addition of alkynes to disilenes with four identical substituents had been studied; the influence of the polarity of the Si=Si double bond, however so slight, on the mechanism of the addition of alkynes was unknown. Thus, the reaction of disilene **1.37** and cyclopropyl alkyne **1.31** was examined (Scheme 4.1).



Scheme 4.1: Reaction of disilene **1.37** with **1.31**.

The reaction of **1.37** with **1.31** afforded four 1:1 cycloadducts. Compounds **2.12** and **2.13** are isomeric disilacyclobutenes. On the basis of the magnitude of the coupling constants between the ring silicons and the vinylic hydrogen, **2.12** and **2.13** have the same regiochemistry, and thus, they are stereoisomers of one another. While the stereoisomers could result from a change in the stereochemistry at any one of the chiral centres of the cyclopropyl ring, the coupling constants of the hydrogens on the cyclopropyl ring in both **2.12** and **2.13** are similar in both isomers, and thus, the stereochemistry about the CH-OMe and CH-Ph groups in the cyclopropyl ring is the same. Notably, in the reaction of **1.4** and **1.29** with alkyne **1.31**, the stereochemistry of the cyclopropyl ring did not change. As such, in the absence of further evidence, we attribute the stereoisomerism of **2.12** and **2.13** to a change in stereochemistry at the chiral silicon atom. Compounds **2.10** and **2.11** are both derived from the ring opening of the

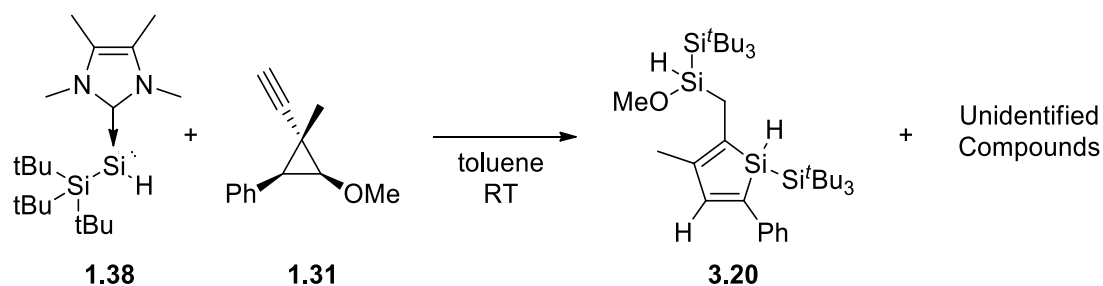
cyclopropyl ring of **1.31**. The regiochemistry of the phenyl and methoxy substituents in **2.10** and **2.11** reveal the nature of the intermediate formed along the reaction pathway: a biradical (Scheme 4.2). This study provides convincing evidence for the formation of a biradical intermediate, which complements the mechanistic studies of disilenes **1.4** and **1.29** with the cyclopropyl alkyne **1.31** and is not consistent with a zwitterionic intermediate as suggested by Scheschkewitz.²



Scheme 4.2: Mechanism of the reaction between cyclopropyl alkyne **1.31** and disilene **1.37**.

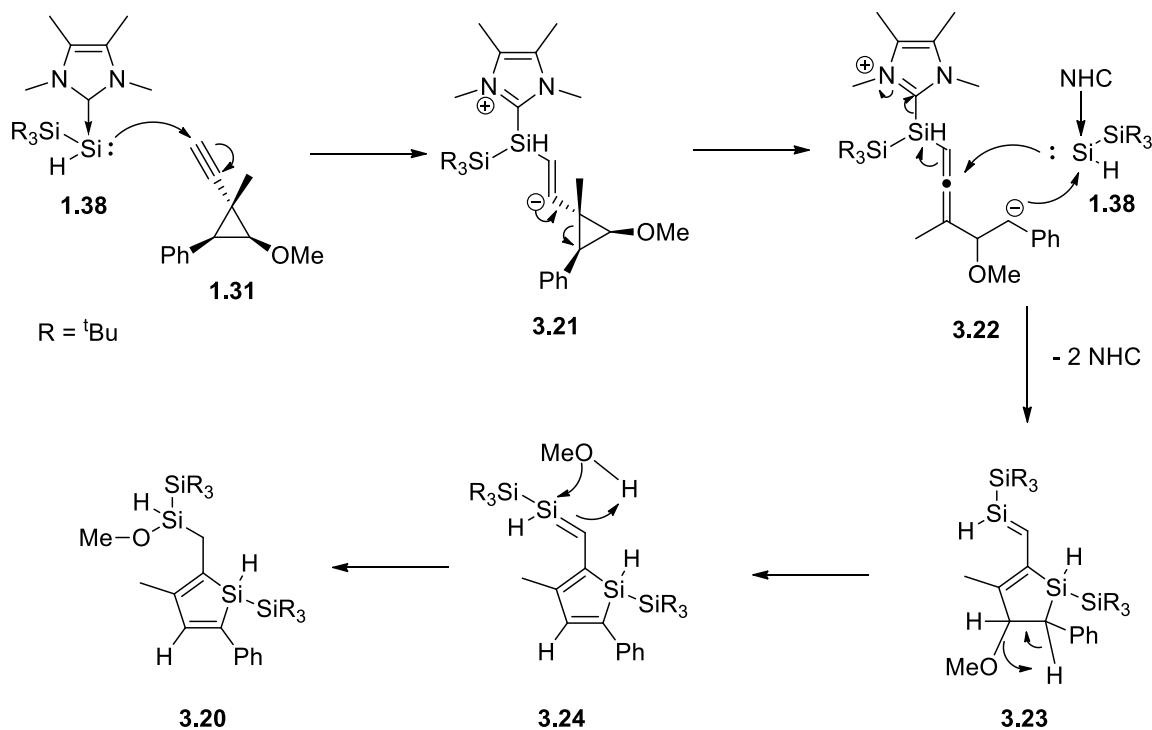
Simple silylenes with sterically bulky dialkyl or diaryl substituents react with alkynes to give silacyclopropenes, where the silylene is believed to act as the electrophile.⁵ The coordination of a Lewis base to silylenes can be used to stabilize silylenes by presumably reducing the electrophilic character of the silylene. Base-

stabilized silylenes exhibit different reactivity than simple silylenes; in particular, the reactivity of disubstituted alkynes with NHC-stabilized silylenes, such as **1.38**, afford siloles and not silacyclopropenes.⁶ The mechanism for the reaction has been proposed to involve a zwitterion generated by the silylene acting as the nucleophile. While this mechanism is supported by DFT computational studies,⁶ there have been no experimental studies to determine the nature of the intermediate. The reaction of silylene **1.38** with cyclopropyl alkyne **1.31** was examined and compound **3.20** was isolated (Scheme 4.3).



Scheme 4.3: Reaction of **1.38** with **1.31**.

Nucleophilic attack of silylene **1.38** at the terminal end of the carbon-carbon triple bond of **1.31** to give a zwitterionic intermediate followed by opening of the cyclopropyl ring toward the phenyl substituent is consistent with the formation of **3.20**. The results provide experimental evidence for the formation of a zwitterionic intermediate as was proposed in the computational study of the reaction.⁶



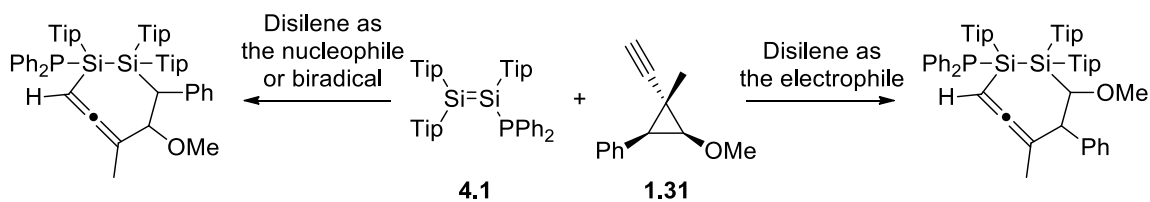
Scheme 4.4: The proposed mechanism for the formation of **3.20**.

The mechanism also revealed the ability of the cyclopropyl ring of **1.31** to open towards the phenyl substituent when a negative charge is present on the α -vinyl carbon. This reactivity was not seen in the vinyl lithium analogues of **1.31**. Protonation of the vinyl lithium reagent derived from **1.31** gave only the cyclopropyl alkene and no ring-opened product. The results have revealed an important aspect of the reactivity of cyclopropyl alkyne **1.31**: ring-opening towards the phenyl group must always be interpreted as a consequence of the formation of a vinylic radical or a negative charge from a zwitterion α to the cyclopropyl ring. To distinguish between these two choices, other factors must be taken into consideration, if possible.

The results presented herein lead to numerous conclusions. First, the addition of alkynes to disilenes, whether symmetrically or unsymmetrically-substituted with aryl or silyl groups, proceeds through a biradical intermediate. Secondly, the formation of a zwitterion with an anion at the α -vinylic carbon derived from **1.31** will open regioselectively toward the phenyl substituent. Lastly, Lewis base-stabilized silylenes act as nucleophiles in the addition to alkynes.

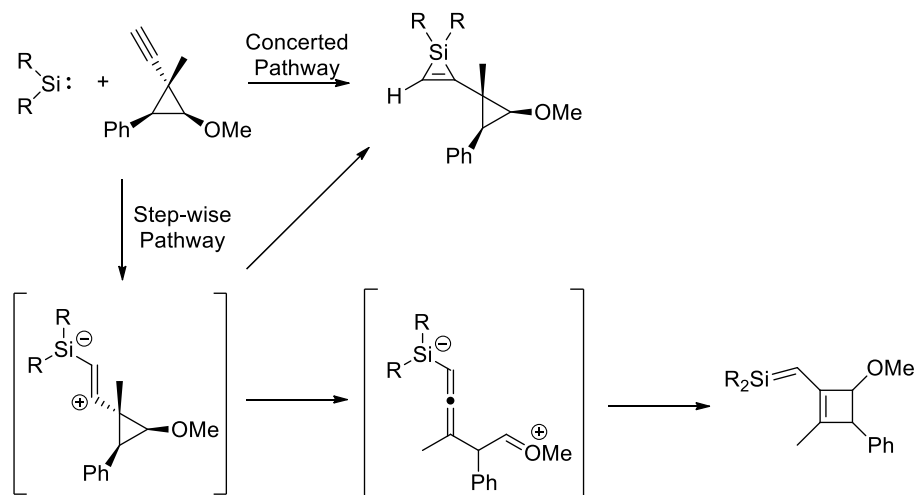
4.2 Future Work

On the basis of the results presented herein, the dipole moment caused by the difference between a Tip group and a Ph group on a Si=Si double bond was not sufficient to alter the nature of the intermediate which is formed in the reaction between alkynes and disilenes. However, with a sufficiently polarized disilene, a change in the nature of the intermediate may be expected. To test this hypothesis, the reaction between alkyne **1.31** and the phosphinodisilene **4.1** should be examined. Disilene **4.1** features one phosphorus and three aryl substituents.⁷ The dipole moment of the Si=Si double bond, as a result of the three aryl substituents and an electron-donating PPh₂ substituent, is expected to be greater than that of disilene **1.37** and, as such, would be an interesting candidate to test for the purported change in mechanism.



Scheme 4.5: The proposed reactivity between the polar disilene **4.1** and alkyne **1.31**.

Also of interest would be the study of the reaction between a simple dialkyl- or diarylsilylene with alkyne **1.31**. On the basis of a computational study, simple silylenes are expected to react as electrophiles with alkynes.⁸ If in the reaction with **1.31** the silylene acted as an electrophile and the reaction was stepwise, then a vinyl cation would be generated next to the cyclopropyl ring and result in regioselective ring-opening toward the methoxy substituent. However, if the reaction is concerted, ring opening is not expected.

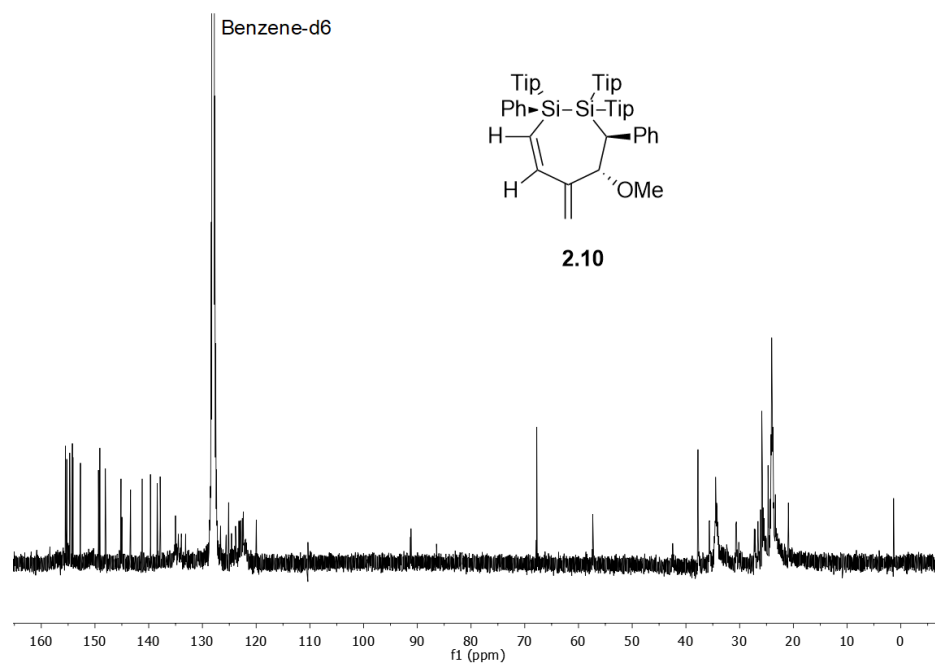
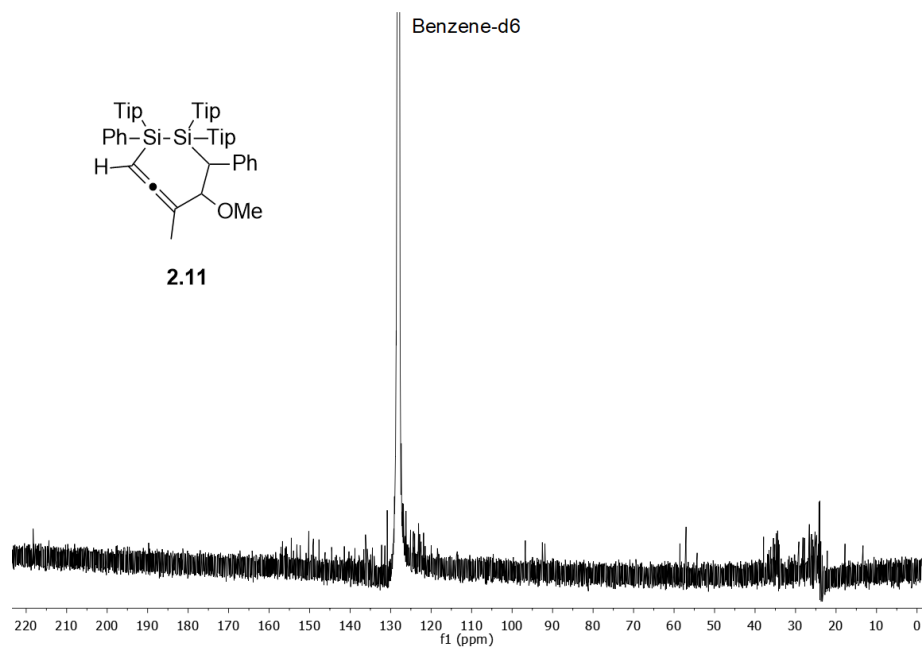


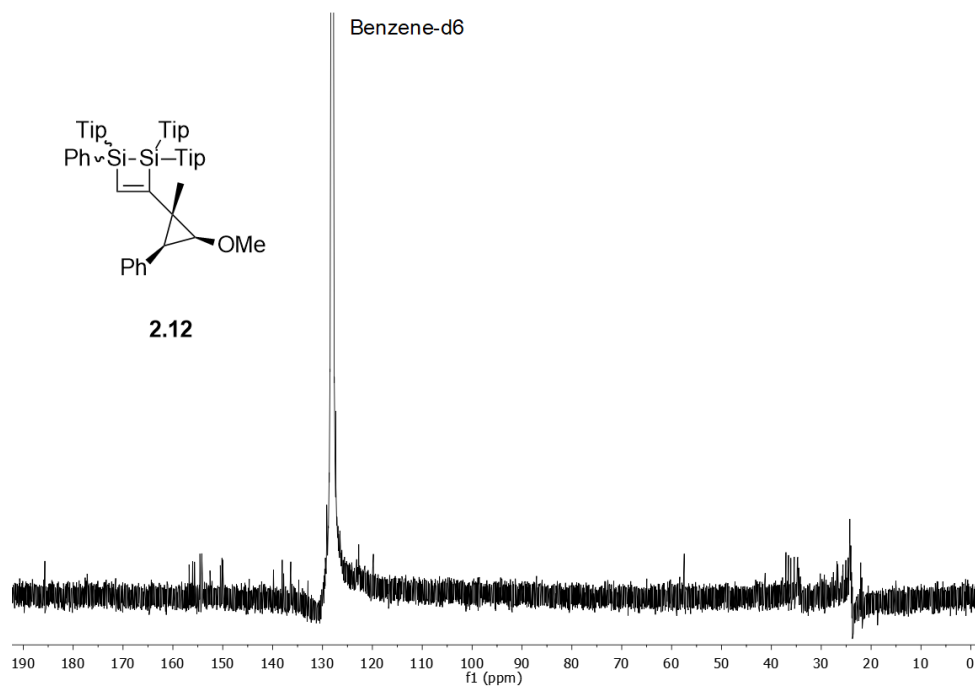
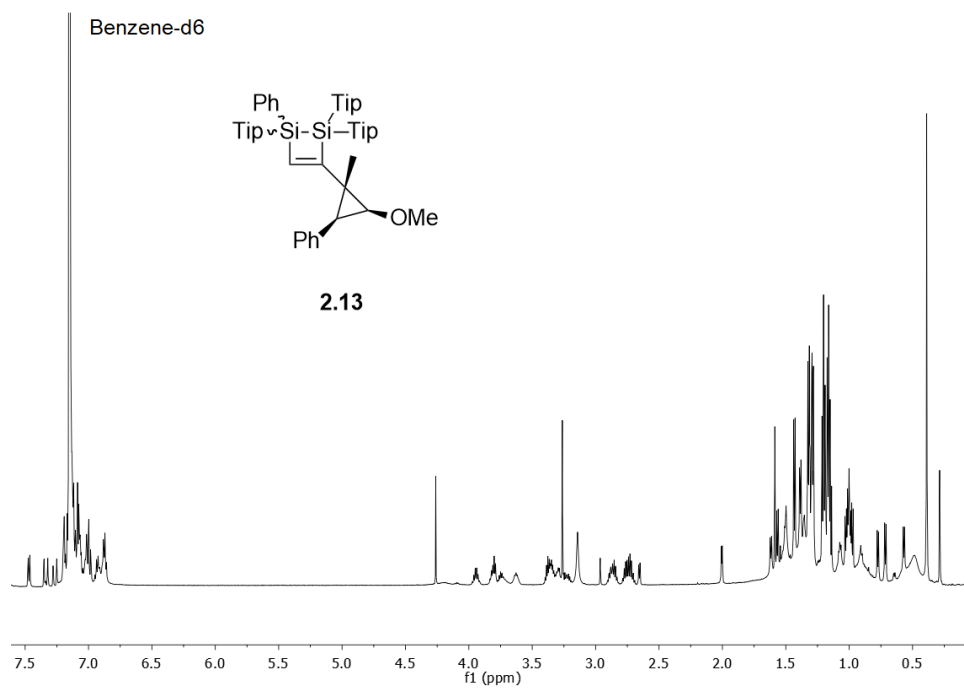
Scheme 4.6: Possible reaction pathways of a simple silylene with alkyne **1.31**.

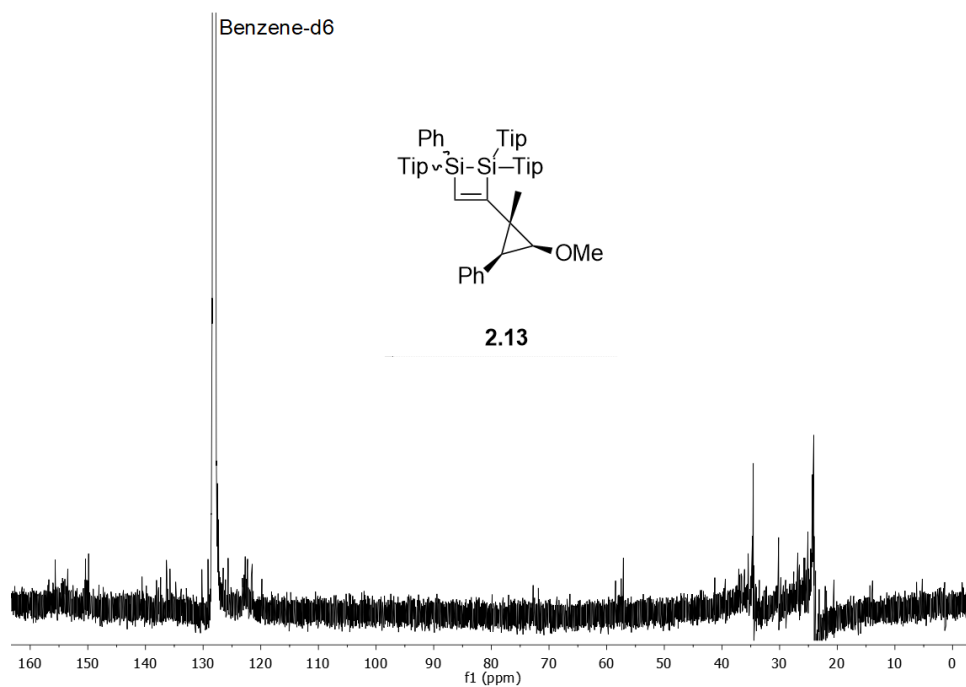
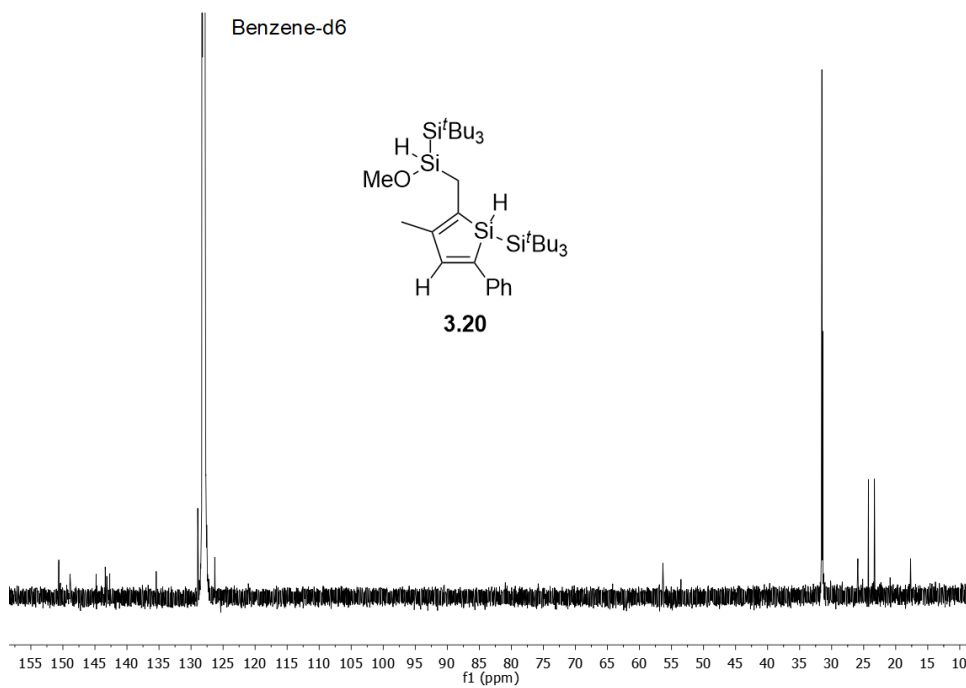
4.3 References

1. Milnes, K. K.; Pavelka, L. C.; Baines, K. M.; *Chem. Soc. Rev.*, **2016**, *45*, 1019.
2. Meltzer, A.; Majumdar, M.; White, A. J. P.; Huch, V.; Scheschkewitz, D.; *Organometallics*, **2013**, *32*, 6844.
3. Majumdar, M.; Bejan, I.; Huch, V.; White, A. J. P.; Whittell, G. R.; Schafer, A.; Manners, I.; Scheschkewitz, D.; *Chem. Eur. J.*, **2014**, *20*, 9225.
4. Gottschling, S. E.; Milnes, K. K.; Jennings, M. C.; Baines, K. M.; *Organometallics*, **2005**, *24*, 3811.
5. Lips, F.; Mansikkamaki, A.; Fettingner, J. C.; Tuononen, H. M.; Power, P. P.; *Organometallics*, **2014**, *33*, 6253.
6. Eisenhut, C.; Szilvsi, T.; Breit, N. C.; Inoue, S.; *Chem. Eur. J.*, **2015**, *21*, 1949.
7. Hartmann, M.; Haji-Abdi, A.; Abersfelder, K.; Haycock, P. R.; White, A. J. P.; Scheschkewitz, D.; *Dalton Trans.*, **2010**, *39*, 9288.
8. a) Koch, R.; Bruhn, T.; Weidenbruch, M.; *Organometallics*, **2004**, *23*, 1570; b) Tanaka, H.; Kondo, Y.; Shoita, Y.; Naka, A.; Ishikawa, M.; Yoshizawa, K.; *Organometallics*, **2011**, *30*, 3160.

Appendices

Appendix A1.1: ^{13}C NMR spectrum (119 MHz, C_6D_6) of **2.10**.**Appendix A1.2:** ^{13}C NMR spectrum (119 MHz, C_6D_6) of **2.11**.

Appendix A1.3: ^{13}C NMR spectrum (119 MHz, C_6D_6) of **2.12**.**Appendix A1.4:** ^1H NMR spectrum (600 MHz, C_6D_6) of **2.13**.

Appendix A1.5: ^{13}C NMR spectrum (119 MHz, C_6D_6) of **2.13**.**Appendix A1.6:** ^{13}C NMR spectrum (119 MHz, C_6D_6) of **3.20**.

Curriculum Vitae

Post-secondary Education and Degrees:	The University of Western Ontario London, Ontario, Canada 2011-2015 B.Sc. Chemistry Thesis Project: Wisner Group
	The University of Western Ontario London, Ontario, Canada Fall 2015-Winter 2018 M.Sc. Chemistry Baines Group
Related Work Experience	Teaching Assistant The University of Western Ontario 2015-2017
	Research Assistant Surface Science Western Summer 2014
Presentations	“Exploring the Reactivity of 1,2,3-azaditetraletine Ring Systems.” Henry, A. H.; Baines, K. M.; 99 th CSC in Halifax, NS June 7, 2016
	“Mechanistic Study of an Asymmetric Disilene” Henry, A. T.; Baines, K. M.; 49 th Inorganic Discussion Weekend, November 12, 2016
	“Mechanistic Study of the Cycloaddition Addition of an Alkyne to an Asymmetric Disilene” Henry A.T., *Baines K.M.; 100 th CSC in Toronto, ON May 30, 2017
	“Addition of Alkynes to a NHC-Stabilized Silylene: A Mechanistic Study” Henry, A. T.; Baines, K. M.; Inoue, S.; 50 th Inorganic Discussion Weekend, November 4, 2017
Course Report	CHEM 9521S – Catalysis – 85%
	CHEM 9603S – Adv. NMR. Spec. II – 92%
	CHEM 9888Y – Crystallography I – 90%
	CHEM 9657 – Seminar – PASS