

SYNTHESIS OF NOVEL CARBENE-STABILIZED SILYLENES AND 1,3,2-
DIAZABOROLE-DERIVED CARBENE COMPLEXES OF BORON

by

HUNTER PATRICK HICKOX

(Under the Direction of Gregory H. Robinson)

ABSTRACT

The investigation of novel silylene ($:\text{SiR}_2$) species is presented herein. The reaction of carbene-stabilized disilicon(0) with one equivalent of $\text{Fe}(\text{CO})_5$ at room temperature yields the carbene-stabilized $\text{Si}_2\text{Fe}(\text{CO})_4$ complex (**72**). Further reaction of **72** with an additional equivalent of $\text{Fe}(\text{CO})_5$ at raised temperatures affords the carbene-stabilized silylene-iron carbonyl cluster, $\text{Si}[\mu\text{-Fe}_2(\text{CO})_6](\mu\text{-CO})\text{Si}$ (**73**), through the insertion of a CO and a $\text{Fe}_2(\text{CO})_6$ unit into the Si=Si double bond. Each silylene center in **73** is covalently bonded to one $\text{Fe}(\text{CO})_3$ center, and datively bonded to the other $\text{Fe}(\text{CO})_3$ using the silicon-based electron lone pair. Notably, compound **73** represents the first example of direct cleavage of a Si=Si double bond by a transition metal species. Subsequently, the reactivity of complex **72** was studied. The reaction of **72** with $\text{HCl}\cdot\text{NC}_5\text{H}_5$ yields a “push-pull” stabilized parent monochlorosilylene $[\text{:Si}(\text{H})\text{Cl}]$ (**78**), with addition of an HCl unit to each silicon atom, and both silicon-based electron lone pairs coordinating a central $\text{Fe}(\text{CO})_3$. Importantly, compound **78** is the first stabilized parent monochlorosilylene isolated at ambient conditions. In addition, the reaction of carbene-stabilized diiodo-bis-silylene with an imidazole-based thiolate ligand in toluene or THF gives a five-membered (**82**) and four-membered (**83**) cyclic silylene *via* unexpected C–H and C–N bond activation, respectively. Compounds **82** and **83**

represent the first cyclic silylenes containing a silicon-silicon bond, and compound **83** is the first example of silicon(I)-mediated C–N bond cleavage of N-heterocyclic carbenes (NHCs). Recently, the synthesis of 1,2-azaborole-derived cyclic (alkyl)(amino)carbene (CAAC)-borane adducts were reported, *via* a 1,2-hydrogen migration. In an effort to extend this chemistry to the diazocycloborole system, we reported the synthesis of 1,3,2-diazaborole-derived NHC-boron halide complexes, *via* a 1,2-hydrogen migration. A reaction of 2-bromo-1,3,2-diazaborole with excess BX_3 ($\text{X} = \text{Br}, \text{I}$) affords the BBr_3 (**87**) and BI_3 (**88**) complexes in quantitative yield (by ^1H NMR). Interestingly, both **87** and **88** are in equilibrium in solution, likely due to the weak electron-donating properties of the 1,3,2-diazaborole-derived carbene. However, the equilibrium of **87** favors the formation of the reactants, while the equilibrium of **88** favors the formation of the products, which could be ascribed to the relative Lewis acidity of BBr_3 when compared to BI_3 .

INDEX WORDS: silylene, N-heterocyclic carbene, disilicon, silicon, “push-pull”, main group, iron carbonyl, monochlorosilylene, bond cleavage, cyclic, boron, borole

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May 2018

DEDICATION

I dedicate this dissertation to my parents, Patrick and Heather Hickox, for their constant love and support and I thank them for helping me to become the person I am today. I would not have made it half this far without them.

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First, I would like to thank my advisor, Dr. Gregory H. Robinson. His mentorship has allowed me the opportunity to become a successful scientist, and his consistent standards have taught me the importance of high-quality work and attention to detail. I would also like to thank my committee members, Dr. Tina T. Salguero, and Dr. Henry F. Schaefer, III, for guiding me throughout my time in graduate school. Thanks especially to Dr. Yuzhong Wang; his instruction in the laboratory has been invaluable, and I would not have enjoyed the success I have had without his support and guidance. Dr. Pingrong Wei has provided his vital X-ray crystallography experience, and Dr. Dongtao Cui has assisted with numerous NMR samples, and these projects could not have been done without their help. Thank you also to the undergrads that I have worked with during my time at UGA, Katie Luedecke, Deidrah Carrillo, and Nathan Dominique; I am grateful for all your help, and I know you all will go on to do great things. I would also like to thank Dr. Melinda Oliver, who showed me that chemistry is exciting and worth pursuing. I would not be where I am without Dr. Oliver's friendship in my early academic years.

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for me. I would be remiss if I did not mention my grandparents. I would like to thank the late Skeet Hickox, who was the hardest working man I have ever met and showed me what can be accomplished when you don't quit. Thanks to the late Ruby Hickox, whose perseverance and grit was only matched by her exceeding kindness. I also want to say thank you to the late Bill Meeks, who's quiet intelligence taught me that listening is oftentimes more valuable than speaking. Of course, I would like to thank Sadie Meeks for her continuing love, and who has shown me that even though you get older, you never have to grow up.

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CHAPTER 1

INTRODUCTION

1.1 Purpose of Study

Oxygen (47%) and silicon (28%) are the two most abundant elements in the earth's crust, occurring primarily as silicate minerals and silica (SiO_2). Moreover, elemental silicon can be obtained by the reduction of SiO_2 . As a semiconductor, silicon offers a cheap and efficient platform to access increasingly advanced electronics.¹ In contrast to the bulk silicon(0) material, molecular compounds containing low-oxidation state silicon are more challenging to access, due to their high reactivity. Silylenes, silicon atoms in the +II oxidation state, represent an important low-oxidation-state organosilicon species. Since the first observation of this transient species, the field of silylene ($:\text{SiR}_2$) chemistry has undergone remarkable developments. Especially, the synthesis of the first stable silylene in 1994² paved the way for silylene utility in both transition metal- and metal-free catalysis.³ Silylenes have also shown promise in small molecule activation (NH_3 , H_2) as well as in C–H bond activation.⁴ The research detailed in this dissertation is largely devoted to studying the novel synthetic routes of silylenes and their transition metal complexes through the carbene-stabilized disilicon(0) platform.

Since the groundbreaking synthesis of the first stable N-heterocyclic carbene (NHC),⁵ NHCs have experienced rapid development,⁶ and have uses in transition metal-⁷ and organocatalysis,⁸ as well as in low-oxidation state main group chemistry.⁹ Additionally, Bertrand reported the synthesis of the first cyclic (alkyl)(amino)carbene (CAAC).¹⁰ With stronger σ -donating and π -accepting capabilities when compared to classical NHCs, CAACs represent an

important class of compounds in carbene chemistry. Many unusual compounds that cannot be stabilized by classical NHCs have been stabilized by CAACs, such as the CAAC-stabilized borylenes.¹¹ Kinjo has recently reported the formation of a carbene center by a boron-initiated 1,2-hydrogen shift in a 1,2-azaborole derivative to give CAAC-BX₃ (X = Cl, Br) complexes.¹² The second focus of this work is the extension of this chemistry to NHCs, showing that a 1,3,2-diazaborole can undergo a boron-mediated 1,2-hydrogen shift to give a 1,3,2-diazaborole-derived carbene complex of a boron trihalide. The development of this project could lead to the formation of a new class of diazaborole-derived NHCs.

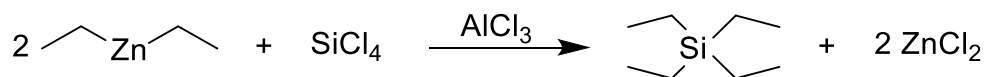
1.2 Organosilicon Chemistry

1.2.1 Historical Perspective

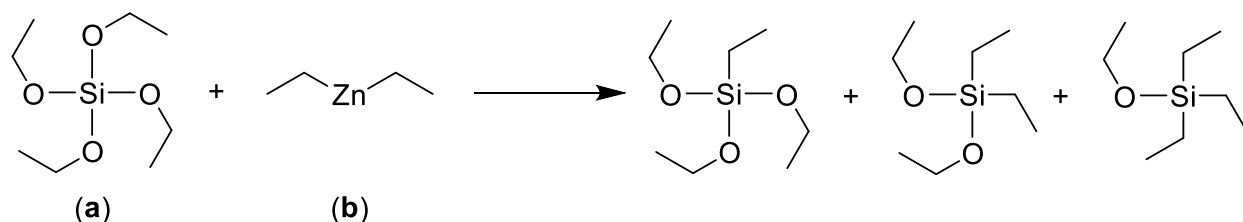
All known life in the universe is carbon-based, although science fiction shows such as *Star Trek* and *Doctor Who* would have us believe that silicon-based life can exist elsewhere. This may not seem like a far stretch for a science fiction writer, as silicon is directly below carbon in group 14. While silicon and carbon may share some similarities, their differences are often the most striking. Though carbon may be the key to life, much of the earth's crust is made up of silicon (28%), as mostly silicates and silica (SiO₂).¹ Silicon is used in numerous practical applications, including concrete, semiconductors, and polymers.¹

In contrast to the long and storied history of organic chemistry, the study of organosilicon compounds is significantly shorter,¹³ as organosilanes are not naturally occurring compounds.¹⁴ Indeed, the first organosilicon compound was synthesized in 1863 by Alsatian Friedel and James Crafts,¹⁵ some fourteen years before their revolutionary work on alkylation of an aromatic hydrocarbon.¹⁶ Friedel and Crafts showed that it was possible to synthesize tetraethylsilane,

(C₂H₅)₄Si, through a reaction of diethyl zinc with silicon tetrachloride (Scheme 1).¹⁵ Subsequently, Albert Ladenburg synthesized the mono-, di-, and tri-functionalized alkoxyethylsilanes by the reaction of (a) with (b) (Scheme 2).¹⁷ However, most known organosilicon compounds during this period were highly reactive, and thus not regarded as particularly useful for synthetic purposes.¹³ Subsequently, this field experienced a significant lull.¹³

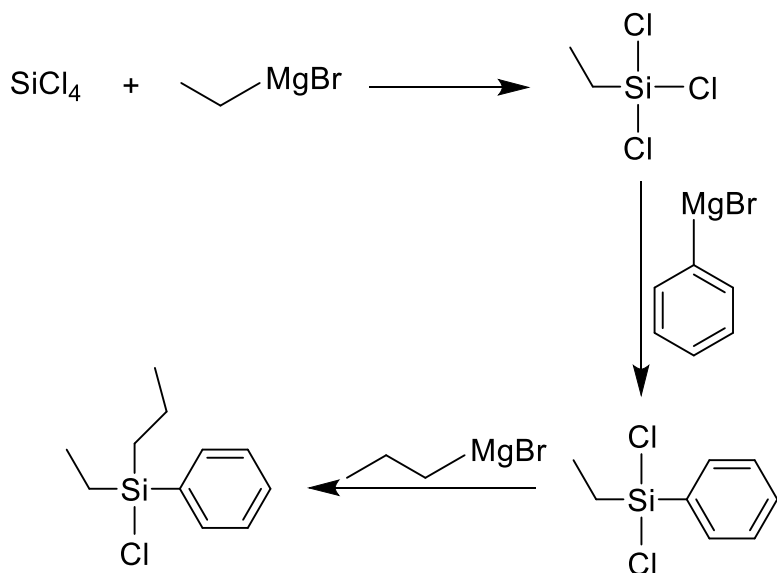


Scheme 1. Synthesis of (C₂H₅)₄Si, the first organosilicon compound.



Scheme 2. Synthesis of mono-, di-, and tri-functionalized alkoxyethylsilanes.

The substantial work of Frederic Kipping between 1899 and 1944 prompted a resurgence in organosilicon chemistry, and detailed the synthesis of numerous novel organosilicon compounds, along with characterization of their elastic and adhesive properties.¹⁸ In 1904, Kipping discovered the Grignard reaction could be utilized in the preparation of organosilanes,¹⁹ which allowed the synthesis of various chloro(alkyl)silanes (Scheme 3).¹⁹⁻²⁰ Additionally, Kipping pioneered the synthesis of silicon-based polymers, but only characterizing them as, “sticky messes of no particular use.”¹⁸ Fortunately, Kipping was incorrect in this particular assessment, as silicone is currently utilized in adhesives, rubber, lubricants, and insulators. For his monumental contributions to laying the foundations of modern organosilicon chemistry, the ACS award in silicon chemistry now bears his name (The Frederic Stanley Kipping Award in Silicon Chemistry).



Scheme 3. Synthesis of mixed alkyl chlorosilanes through multiple Grignard reactions.

Despite Kipping's considerable impact on organosilicon chemistry, carbon and silicon were seen as largely similar in their chemical properties.¹³ However, Walter Diltthey was the first to show that silicon could exist in a hexacoordinate environment, in stark contrast to the strictly tetracoordinate carbon (Figure 1).²¹ Nearly forty years passed after Diltthey's discovery and the next major advancement in organosilicon chemistry. Indeed, these large intervals of time between breakthroughs in organosilicon chemistry highlight the difficulty of the field when compared to classical organic chemistry.

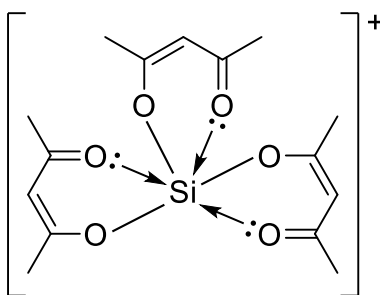
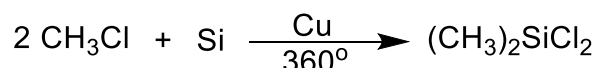
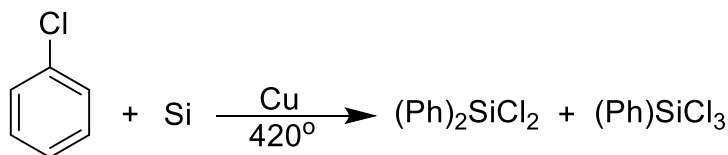


Figure 1. Hexavalent silicon cation.

Eugene Rochow and Richard Müller simultaneously developed the first direct preparation of methyl- and phenylchlorosilanes, without the use of a Grignard reagent.²²⁻²⁵ Working at General Electric in the United States in 1941, Rochow reported the reaction of elemental silicon with the corresponding alkyl halides, in the presence of a copper catalyst, at high temperatures gave the alkylchlorosilanes directly (Scheme 4).²²⁻²⁴ Richard Müller began developing this technique concurrently in Germany, but exact dates are unknown due to a secrecy restriction placed by the German government.²⁵ This process is a high-yield synthesis for both alkyl- and aryl-silanes, though a silver catalyst was preferred for the synthesis of an aryl-silane (Scheme 5).²⁴ Modified versions of the Müller-Rochow synthesis are still used to synthesize the precursors to silicones at an industrial level.²⁶ Following the seminal work by Müller and Rochow, organosilanes became much more widely available, although initially, the number of available alkylsilanes was sparse.¹ Since the 1940's, organosilicon compounds have been extensively utilized in organic, analytical, materials, and inorganic chemistry.²⁷



Scheme 4. Synthesis of dichlorodimethylsilane.

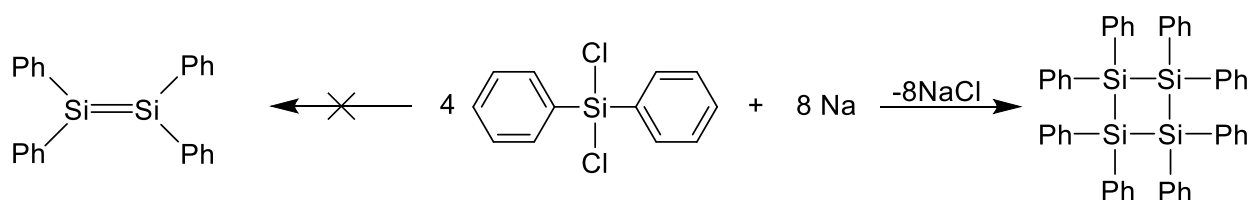


Scheme 5. Synthesis of aryl-silanes.

1.2.2 Compounds Containing Silicon-Silicon Multiple Bonds

While compounds containing carbon multiple bonds (*i.e.*, C=C, C=O, etc.) have been studied for centuries, multiply bonded silicon species (*i.e.*, Si=Si, Si=C, Si=O) are historically

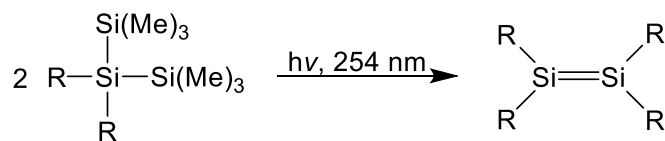
much less predominant. Multiply bonded species of the heavier group 14 elements were thought to be synthetically inaccessible, due to the ‘double bond rule’.²⁸ Chemists believed that elements with a principle quantum number of $n > 2$ could not form multiple bonds because of considerable Pauli repulsion between the electrons of the inner shells.²⁸ Kipping supposed he had isolated the first disilene in 1927 ($\text{Ph}_2\text{Si}=\text{SiPh}_2$) through the sodium reduction of diphenyldichlorosilane (Ph_2SiCl_2).²⁹ However, it was later proved that Kipping isolated the dimer, octaphenylcyclotetrasilane (*cyclo*- $[\text{Si}_4\text{Ph}_8]$) (Scheme 6).³⁰ In his *Bakerian Lecture on The Organic Derivatives of Silicon*, Kipping proclaimed that multiple bonds to silicon atoms would ‘likely be very unstable and the results of their investigation of little importance’ due to the ‘double bond rule’.²⁰ However, several transient disilenes were observed and studied over the next decades.^{1, 31}



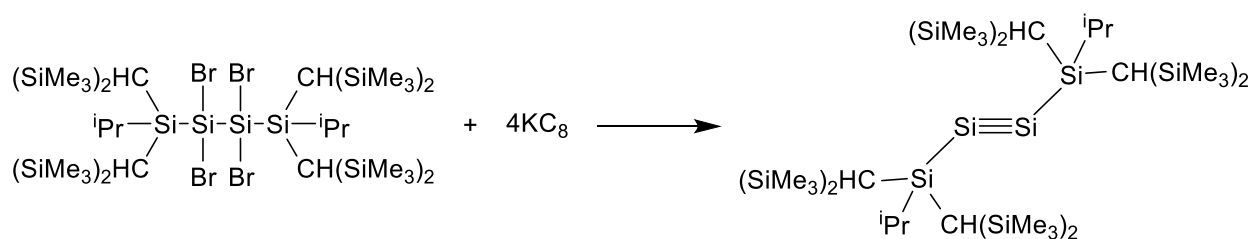
Scheme 6. Failed synthesis tetraphenyldisilene, and synthesis of *cyclo*-(Si₄Ph₈) (Ph = phenyl).

The first stable disilene ($\text{R}_2\text{Si}=\text{SiR}_2$) was isolated in 1981 by Robert West.³² West showed that the photolysis of a trisilane yielded the first disilene ($\text{Mes}_2\text{Si}=\text{SiMes}_2$, Mes = 2,4,6-trimethylphenyl), likely through the formation of the dimesityl silylene ($\text{Mes}_2\text{Si:}$) (Scheme 7). Currently, more than 70 disilenes with different bonding modes have been reported.³³ While the synthesis of disilenes has proved to be possible, organosilicon chemistry still poses challenging synthetic obstacles. Indicative of this difficulty, the first transient disilyne was reported in 1986, but only observed as a reactive intermediate,³⁴ and the first stable disilyne ($\text{RSi}\equiv\text{SiR}$, where R is a sterically demanding ligand) was isolated in 2004 by Sekiguchi.³⁵ Reduction of 2,2,3,3-tetrabromo-1,1,4,4-tetrakis[bis(trimethylsilyl)methyl]-1,4-diisopropyltetrasilane with four

equivalents of potassium graphite gives the stable disilyne (Scheme 8). The bulky silyl substituents provide both kinetic and thermodynamic stability. The discoveries of the disilene and disilyne underscore the challenges that modern silicon chemists face.

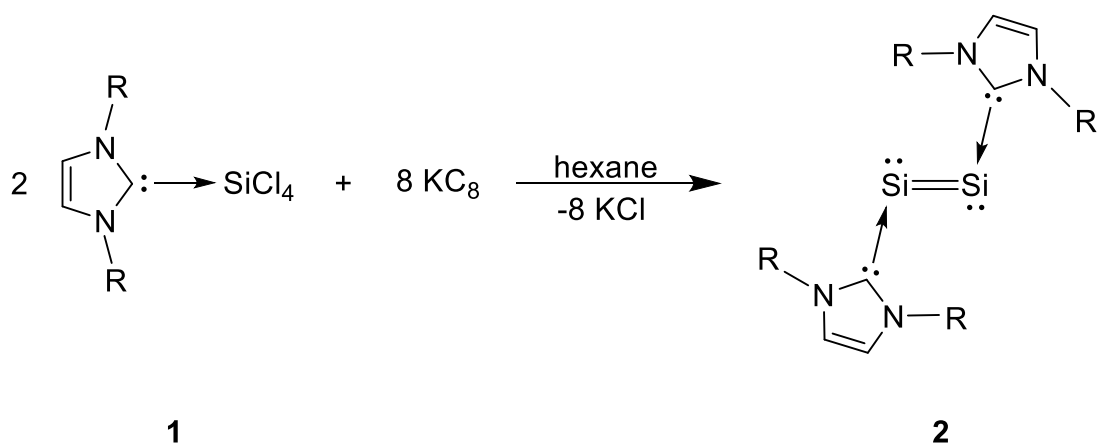


Scheme 7. Synthesis of the first disilene (R = mesityl).



Scheme 8. Synthesis of the first disilyne (iPr = isopropyl).

In 2008, the Robinson group reported the synthesis of carbene-stabilized disilicon(0), a stable compound with a Si=Si double bond, with both silicon atoms in the zero oxidation state.³⁶ The reaction of N-heterocyclic carbene-SiCl₄ complex (**1**) with four equivalents of potassium graphite yields carbene-stabilized disilicon(0) (**2**) (23.2% yield) (Scheme 9). The central Si₂ core in **2** provides a unique platform to access Si(0) chemistry, as both silicon atoms also possess a silicon-based electron lone pair.



Scheme 9. Synthesis of carbene-stabilized disilicon(0) (R = 2,6-diisopropylphenyl).

1.2.3 Electronic Structure of Silicon-Silicon Multiple Bonds

The structure and bonding of alkenes ($R_2C=CR_2$) and alkynes ($RC\equiv CR$) has been thoroughly studied and is a central pillar of organic chemistry. The $C=C$ double bond is composed of one σ -bond, formed by the overlap of one sp^2 -hybrid orbital of each carbon atom, and one π -bond, formed by the overlap of one $2p$ -orbital of each carbon atom. This leads to an ideal $R-C=C$ angle of 120° . The $C\equiv C$ triple bond is formed by the overlap of the sp -orbitals of two carbon atoms containing two orthogonal π -bonds.³⁷ It is noteworthy that the geometries of both disilenes and disilynes are in stark contrast to that of alkenes and alkynes, respectively, as both disilenes and disilynes typically adopt a *trans*-bent geometry around the silicon centers.^{33, 38}

The $C=C$ double bond in alkenes can be thought of as the interaction between two triplet carbenes, forming two covalent bonds (**a**, Figure 2). In comparison, the singlet-triplet energy gap for silylenes is much higher than for carbenes, so divalent silicon favors the singlet ground state. This prevents the lone pairs of the singlet silylenes from interacting in a classical way, as there is substantial Pauli repulsion (**b**, Figure 2). Instead, the lone pairs of each silicon atom are inclined to interact with an empty p -orbital of the adjacent silicon atom, leading to the *trans*-bent geometry

commonly found in disilenes (**c**, Figure 2). Indeed, this *trans*-bent geometry is also present for the remainder of the heavier group 14 alkene analogs. Interestingly, the planar geometry of alkenes is not the standard for the doubly bonded species of the group 14 elements, but rather the exception.^{1,}

33, 38

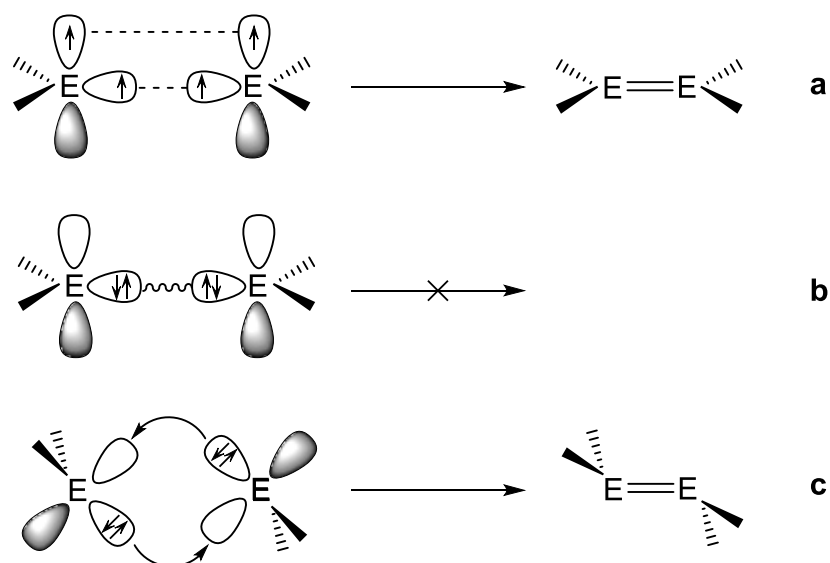


Figure 2. MO model of triplet-triplet (**a**) and singlet-singlet (**b**, **c**) interaction of doubly bonded group 14 elements. a) E = C; b,c) E = Si, Ge, Sn, Pb.

An alternate explanation for the *trans*-bent geometry of disilenes is the mixing of the silicon-silicon π - and σ^* -orbitals. This stabilization is only possible because of the bending at the silicon centers. In general, a larger π - σ^* interaction results in a more pronounced *trans*-bent geometry (Figure 3). In addition to the π - σ^* orbital mixing, electronegativity of the substituents can have an effect on the degree of *trans*-bending. Electron-accepting substituents (-F, -OH, -NH₂) increase the singlet-triplet energy gap, which increases the amount of *trans*-bending, and electron donating substituents (-BH₂, -SiH₃) decrease the singlet-triplet energy gap, reducing the degree of *trans*-bending.^{33, 38}

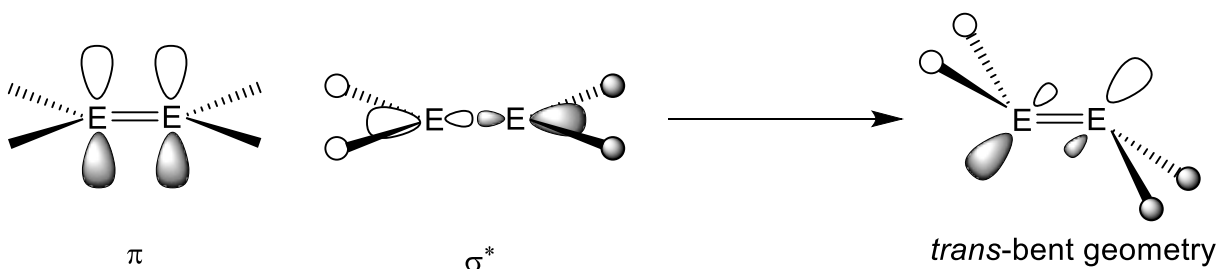


Figure 3. π - σ^* orbital interactions of doubly bonded group 14 elements (*i.e.*, E, excluding carbon).

1.3 Stable Silylenes

1.3.1 Historical Overview of Silylenes

Two electronic configurations, the triplet state, and the singlet state, dominate the chemistry of the divalent group 14 species ($:ER_2$). The parent carbene, $:CH_2$, exists in a triplet ground state, with two unpaired electrons. The triplet parent carbene can be thought to exist as a biradical, with one electron in the p_π orbital, and one electron occupying the σ frontier orbital.³⁹ Electronic configuration of carbenes will be discussed more thoroughly in a later section. In comparison, the parent silylene, $:SiH_2$, exists as a ground state singlet (Figure 4), with both electrons occupying the lower energy sp^2 -hybridized orbital, giving a bent geometry. The differentiation between the parent carbene and parent silylene may be due to the smaller HOMO-LUMO gap for $:CH_2$ (27 kcal/mol) than for $:SiH_2$ (52 kcal/mol).³⁸ Triplet silylenes are highly reactive and were first observed in 2003 by Sekiguchi using low-temperature matrix isolation.⁴⁰

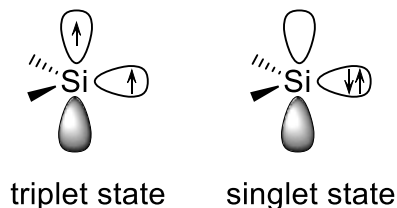


Figure 4. Electronic representation of the triplet and singlet states of a silylene.

Substituents may play a large role in the stabilization of silylenes. Work by Apeloig has shown that electron donating substituents ($-\text{NH}_2$, $-\text{OH}$, $-\text{SH}$) can donate electron density to the empty 3p-orbital on the silicon atom, increasing the energy level of the LUMO, thereby increasing the HOMO-LUMO gap.⁴¹⁻⁴² The resulting blue shift of the absorbance maxima in the UV absorbance spectrum that was predicted computationally was observed for several silylenes with electron donating substituents. In contrast, vinyl and phenyl substituents give a red shift in the absorbance maxima, due to a lower energy LUMO caused by interactions between the π orbital of the substituent and the empty 3p orbitals on the silicon atom. This π -3p orbital interaction explains the relative stability of the N-heterocyclic silylenes compared to alkyl silylenes, as two nitrogen atoms in the heterocycle can donate electron density to the empty 3p orbital on the silicon atom.⁴¹⁻⁴² Additionally, unsaturated N-heterocyclic silylenes can exhibit some degree of aromaticity, which contributes somewhat to the overall stability (due to the well-known effects of the aromatic stabilization energy).¹

In addition to electronic effects, sterically bulky substituents can have a significant effect on the HOMO-LUMO energy gap. Wider R-Si-R (R = substituent) angles are more prevalent for silylenes in the triplet ground state, while smaller angles are seen more commonly in the singlet ground state. An increased steric bulk of the substituents leads to a smaller HOMO-LUMO gap, causing the absorbance maxima of the UV spectrum to become more red shifted. Indeed, Apeloig reported a red shift in the absorbance maxima for multiple silylenes with bulky substituents, and a blue shift in the absorbance maxima for silylenes with smaller steric effects.³⁸

The singlet silylene contains two reactivity sites. The filled sp^2 hybridized orbital can act as a Lewis base, and perform a nucleophilic attack on an electrophile, while the empty p orbitals on the silicon atom can act as a Lewis acid, accepting electrons from an electron-rich donor. These

properties have been critical in the “push-pull” stabilization of several transient silylenes.⁴³⁻⁴⁴ Much like carbenes, these simple ambiphilic silylenes can insert into σ -bonds (Figure 5), as well as undergo cycloaddition to π -bonds.³⁸

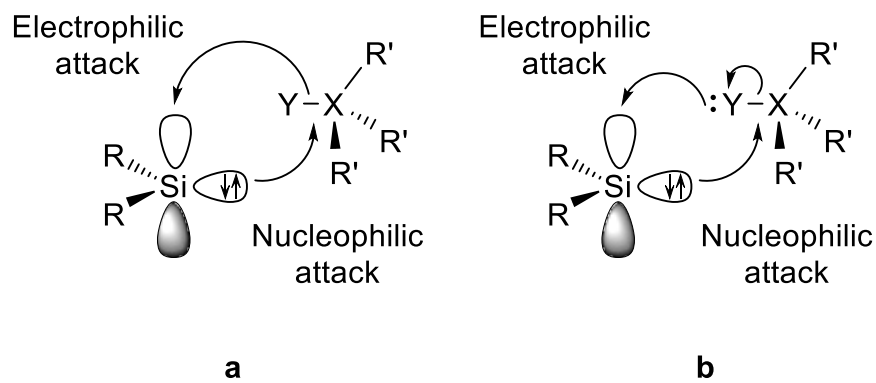
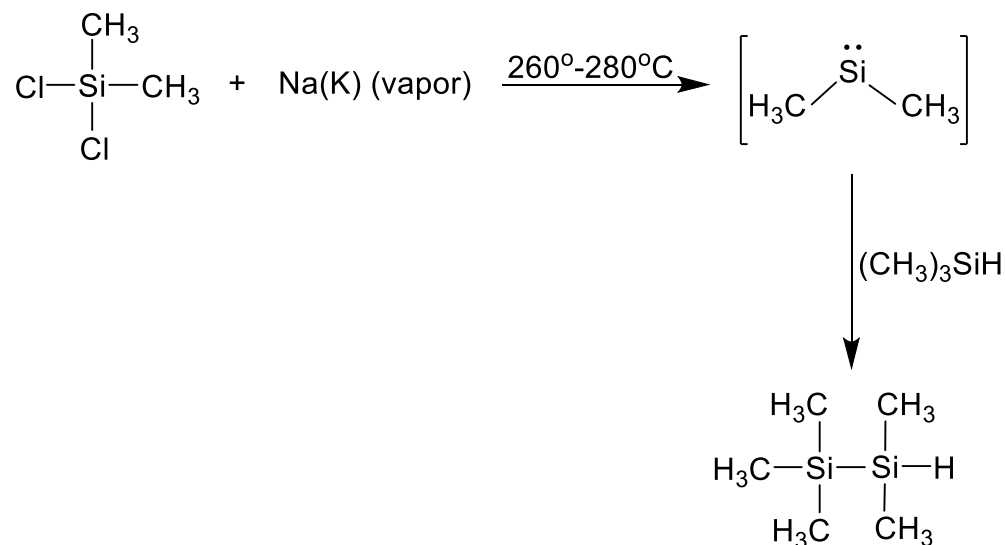


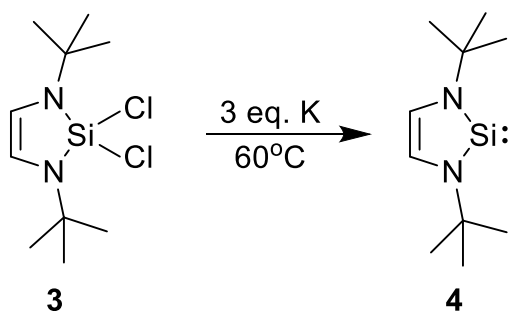
Figure 5. Insertion of silylenes into σ -bonds: **(a)** Initial $\sigma_{\text{X-Y}} - \text{p}_{\text{Si}}$ interaction. **(b)** Initial $n_{\text{Y}} - \text{p}_{\text{Si}}$ interaction.

As with many highly reactive species, silylenes were initially reported as transient reaction intermediates. In 1964, Skell and Goldstein detailed the generation of dimethylsilylene in the gas phase at 260°C-280°C through the reaction of dichlorodimethylsilane with sodium-potassium vapor under inert atmosphere (Scheme 10).⁴⁵ However, silylenes would remain an elusive reaction intermediate for the next 30 years, only stabilized in matrices.⁴⁶ Indeed, when West and coworkers synthesized the first disilene ($\text{R}_2\text{Si}=\text{SiR}_2$) in 1981, they also reported the low-temperature capture of dimesityl-, dimethyl-, diethyl-, and phenylmethylsilylenes in argon matrices.³² Notably, the first two-coordinate silicon compound stable at ambient conditions, the silocenocene $[(\eta^5\text{-Me}_5\text{C}_5)_2\text{Si}]$, was synthesized by Jutzi.⁴⁷



Scheme 10. Proposed synthesis of dimethylsilylene.

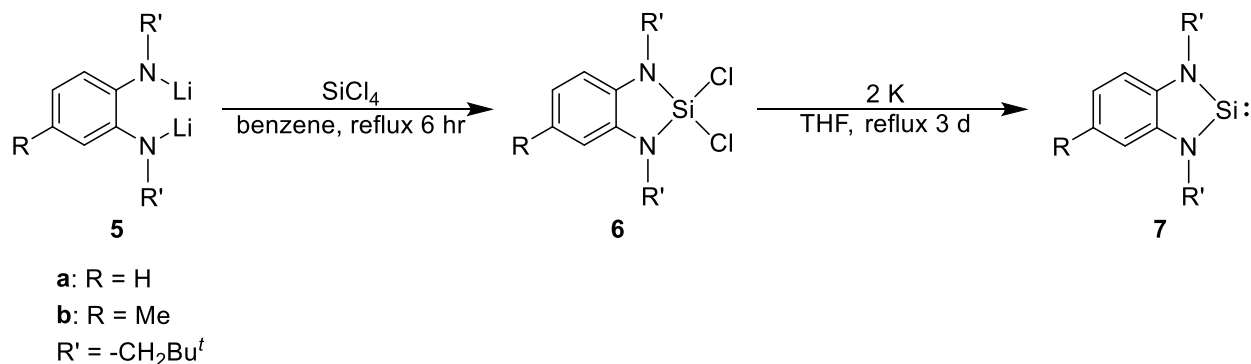
The hunt for the elusive silylene was still on, as the synthesis of the first stable carbene in 1991⁵ marked the isolation of all but one of the divalent group 14 species (*i.e.*, R₂E:). The stable germylene (R₂Ge:), stannylene (R₂Sn:), and plumbylene (R₂Pb:) were synthesized by Lappert in 1976.⁴⁸⁻⁴⁹ Robert West and Michael Dink isolated the first silylene stable at ambient conditions (**4**) in 1994, by reduction of dichloro-N-heterocyclic silane (**3**) with potassium metal at elevated temperatures (Scheme 11).² In stark contrast to previous reports of silylene reactivity, this five-membered cyclic silylene was quite unreactive, exhibiting no reactivity with pyridine, trimethylphosphine, triethylamine, or THF, which were all known to form Lewis acid-base complexes with silylenes.² The saturated analog was synthesized by West and Dink two years later.⁵⁰ Investigations into N-heterocyclic silylenes have found uses in catalysis,⁵¹⁻⁵² as well as in the coordination of transition metal compounds.^{4, 52}



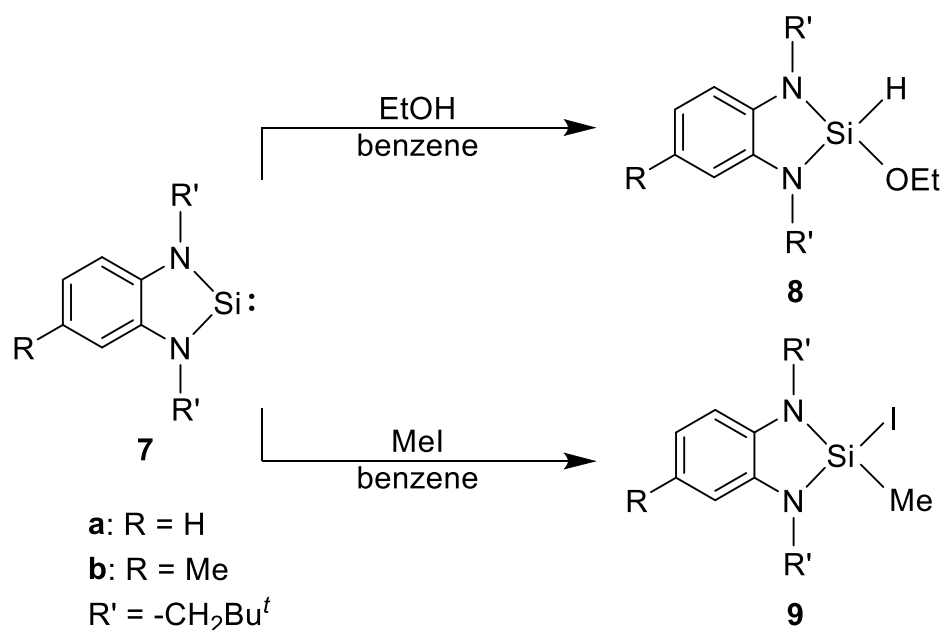
Scheme 11. Synthesis of the first stable silylene (**4**).

1.3.2 Cyclic Silylenes

In addition to the unsaturated N-heterocyclic silylene (**4**), several other notable cyclic silylenes were reported. Lappert and Gehrhus isolated two benzo-fused silylenes.⁵³ The N,N'-dineopentyl-*o*-phenylenediamidodilithium compounds (**5a-5b**) were treated with silicon tetrachloride to give the bis(amino)-dichlorosilanes (**6**). The silicon atoms in **6a** and **6b** were reduced with potassium metal in boiling THF to give the stable bis(amino)silylenes **7a** and **7b** (Scheme 12). In contrast to **4**, **7** displayed promising reactive capabilities, as oxidative addition of ethanol or iodomethane to **7** rapidly produces the two corresponding products, **8a**, **8b**, **9a**, and **9b** (Scheme 13).

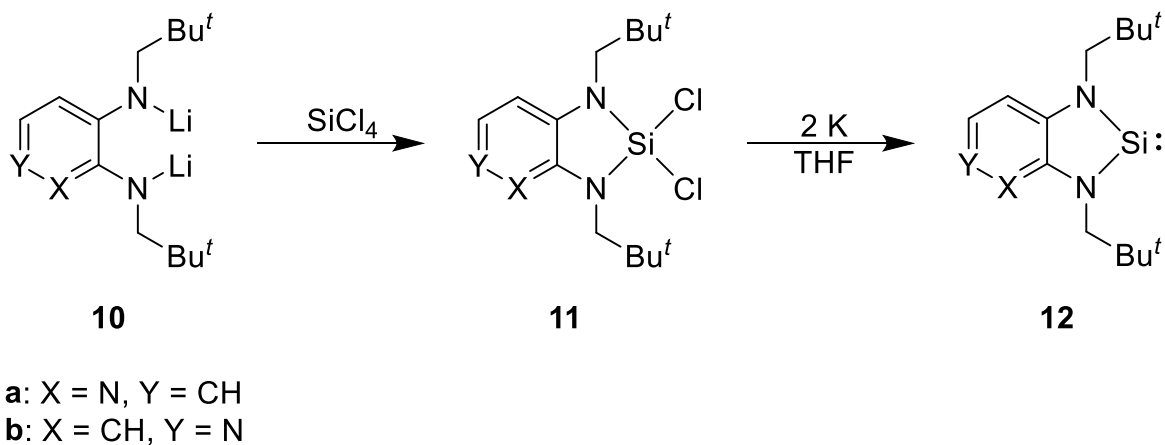


Scheme 12. Synthesis of compounds **6** and **7**.



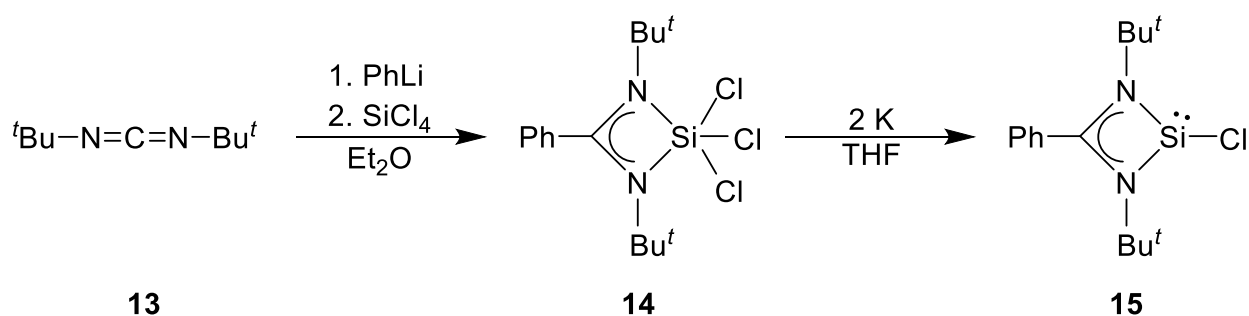
Scheme 13. Oxidative addition of EtOH and MeI to compound **7**.

Heinicke isolated the pyrido-fused analog of compound **7**. Reaction of dilithium pyridine-2,3-diamide (**10**) with silicon tetrachloride affords the cyclic diaminodichlorosilane (**11**), which was reduced by potassium in THF to give the 1,3-dineopentylpyrido[*b*]-1,3,2λ²-diazasilole (**12**) (Scheme 14).⁵⁴ Compound **12** also readily prompted oxidative addition, as any amount of water or an alcohol yielded the corresponding hydridosilicon(IV) compounds. It is of note that the stannylene and germylene analogs of **12** were also isolated.⁵⁴



Scheme 14. Preparation of compound **12**.

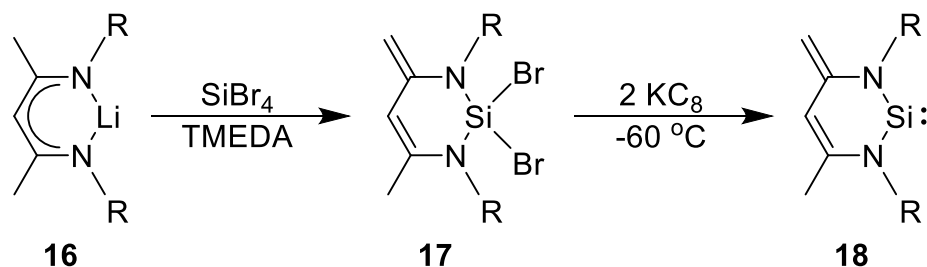
Roesky detailed the synthesis of the first monomeric four-membered cyclic chlorosilylene complex.⁵⁵ Reaction of *tert*-butylcarbodiimide (**13**) with PhLi and subsequent treatment with silicon tetrachloride yields the chlorosilane [PhC(N*t*Bu)₂]SiCl₃ (**14**).⁵⁵ Further reaction of **14** with potassium metal in THF gives the monomeric chlorosilylene [PhC(N*t*Bu)₂]SiCl (**15**) in 10% yield (Scheme 15). The amidinate ligand bonding mode towards the silicon atom resembles that of an *N,N'*-chelating ligand. The silicon atom resides in a distorted trigonal planar geometry (the sum of the bond angles at the silicon center = 260.73°), which is significantly smaller than the 330.0° angle found in the tetra-coordinated silylene [(SiMe₃)C(PMe₂)₂]₂Si.⁵⁶ This difference in angles suggests the presence of a silicon-based electron lone pair in **15**.



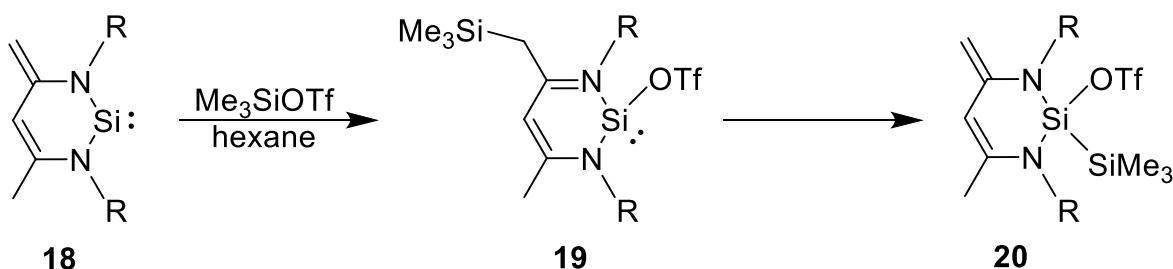
Scheme 15. Preparation of silylene **15**.

The formation of a six-membered N-heterocyclic silylene with ‘ambivalent reactivity’ towards electrophiles was also reported.⁵⁷ Reaction of compound **16** with silicon tetrabromide and TMEDA yields the dibromosilyl complex **17** (Scheme 16). Reduction of **17** with potassium graphite in THF at -60 °C gives the N-heterocyclic silylene (**18**). Further reaction of compound **18** with Me₃SiOTf gives compound **19** (Scheme 17). **19** is the kinetic product of this reaction and slowly isomerizes to give the thermodynamic product, compound **20** (molar ratio of **19:20** is about 2:3 after four days). Interestingly, **18** is involved in the metal-free activation of several small

molecules, including NH_3 ,⁵⁸ acetylene,⁵⁹ haloalkanes,⁶⁰ N_2O ,⁶¹ O_2 ,⁶² CO_2 ,⁶³ and elemental sulfur, selenium, and tellurium.⁶⁴

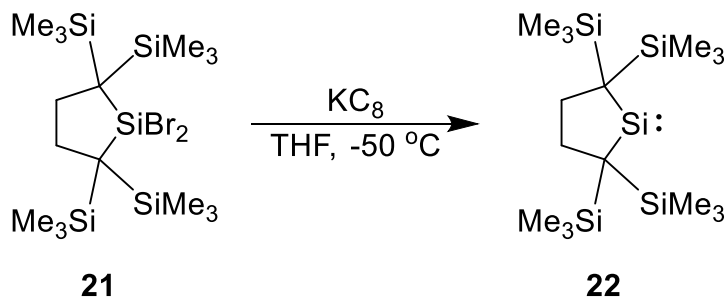


Scheme 16. Synthesis of compound **18** (R = 2,6-diisopropylphenyl).



Scheme 17. Reaction of compound **18** with Me_3SiOTf , and slow isomerization of **19** to **20** (OTf = OSO_2CF_3) (R = 2,6-diisopropylphenyl) .

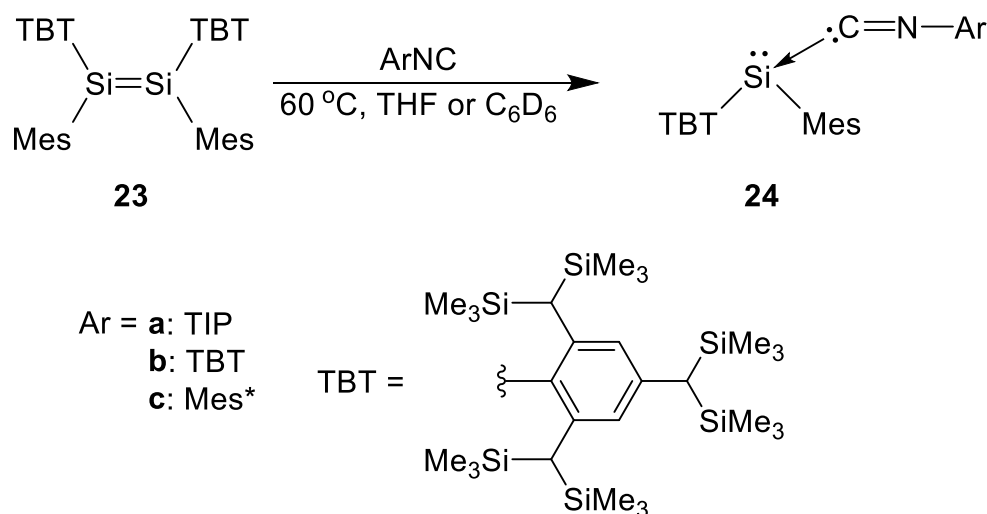
Notably, Kira reported the first stable cyclic dialkylsilylene (**22**)⁶⁵ by reducing cyclic dibromosilane (**21**) with potassium graphite in THF at $-50\text{ }^\circ\text{C}$ (Scheme 18). Dialkylsilylene **22** is much less stable than N-heterocyclic silylenes, due to the lack of electronically stabilizing nitrogen atoms adjacent to the silylene center. The stability of this cyclic silylene is instead provided by the sterically bulky ancillary groups, which prevent dimerization. Indeed, this compound was stored for a short time at $0\text{ }^\circ\text{C}$, but slowly decomposed to the corresponding silaethane. Interestingly, this decomposition does not occur for the corresponding stannylene⁶⁶ and germylene⁶⁷ analogs.



Scheme 18. Synthesis of dialkylsilylene **22**.

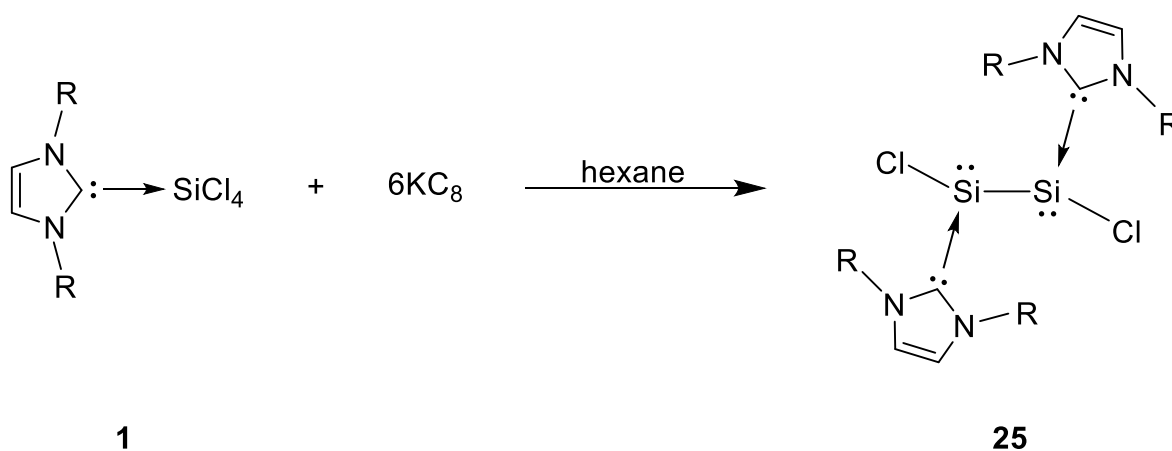
1.3.3 Three Coordinate Acyclic Silylenes

While cyclic silylenes comprise the majority of silylene chemistry, acyclic silylenes are also of great interest.⁶⁸ Lacking the steric or electronic stabilizing effects from a heterocycle, acyclic silylenes typically rely on Lewis-base stabilization. Tokitoh *et al.* synthesized the first stable silylene-Lewis base complex.⁶⁹ The use of a significantly sterically bulky protecting group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (TBT), on disilene **23** provides an increased level of stability (Scheme 19). Upon heating, disilene **23** dissociates into the corresponding silylene in solution, which can be coordinated *in situ* by an isocyanide, giving compound **24** (Scheme 19). Compound **24** is highly sensitive and decomposes readily in the presence of trace moisture or reduced heat. Consequently, single crystal X-ray structures were not achieved.



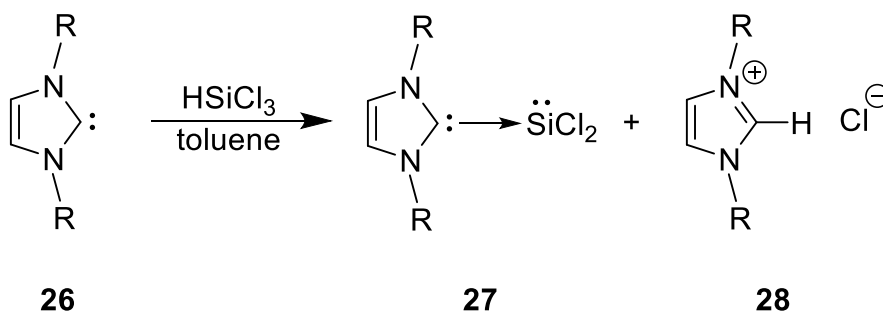
Scheme 19. Synthesis of silylene-isocyanide complexes **24a-c** (Mes = mesityl, Mes* = 1,3,5-tert-butylbenzyl).

In 2008, the Robinson group reported the synthesis of an N-heterocyclic carbene-stabilized dichloro-bis-silylene.³⁶ Reduction of the NHC-SiCl₄ adduct (**1**) with potassium graphite yields the carbene-stabilized bis-silylene **25** (Scheme 20). The (Cl)Si-Si(Cl) core of **25** is sterically protected by the bulky carbene ligands, and each silicon atom is in the formal +1 oxidation state. Both silicon atoms exist in a distorted trigonal pyramidal geometry, with a gauche configuration in the Si₂Cl₂ core, to accommodate for the substantial steric effects of the silicon-based electron lone pair. Each silylene center is stabilized by an N-heterocyclic carbene and covalently bonded to a chloride and the other silylene center, giving a three-coordinate acyclic silylene. Notably, Filippou recently reported a synthesis for L:(X)Si-Si(X):L (X = Cl, Br, I), by reaction of carbene-stabilized disilicon(0) (L:Si=Si:L, L: = C{N(2,6-Prⁱ₂C₆H₃)CH}₂) with 1,2-dihaloethanes.⁷⁰

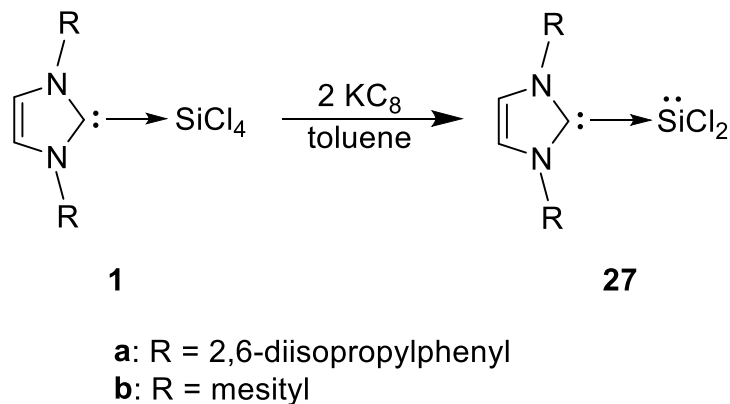


Scheme 20. Synthesis of carbene-stabilized bis-silylene, **25** (R = 2,6-diisopropylphenyl).

Following the report by Robinson, an N-heterocyclic carbene-stabilized dichlorosilylene ($:\text{SiCl}_2$) was achieved.⁷¹ Reductive elimination of HCl from trichlorosilane in the presence of NHC yields the carbene-stabilized dichlorosilylene, **27**, in high yield (79%) (Scheme 21). The insoluble NHC-HCl salt (**28**) is precipitated and can be recovered from the original toluene solution. Compound **27** may also be achieved by the potassium graphite reduction of the NHC- SiCl_4 complex (68% yield) (Scheme 22). The silicon atom in **27** exists in a distorted trigonal pyramidal geometry, to afford significant steric space for the silicon-based lone pair.

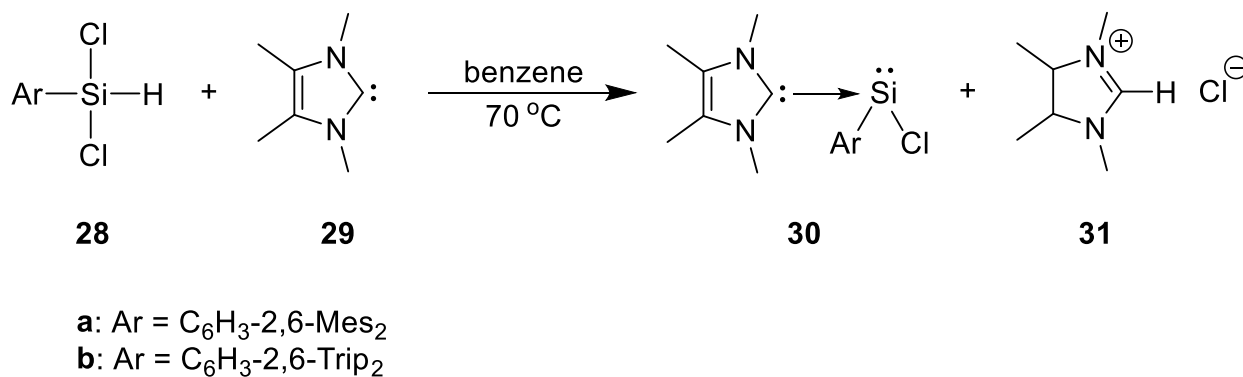


Scheme 21. Synthesis of dichlorosilylene, **27** (R = 2,6-diisopropylphenyl).



Scheme 22. Alternate synthesis of compound **27**.

In 2010,⁷² Filippou synthesized an N-heterocyclic carbene adduct of an arylchlorosilylene (**30**) by combining the arylchlorosilane (**28**) with two equivalents of NHC (**29**) in benzene at raised temperatures (Scheme 23). The NHC-HCl salt (**31**) precipitates out of benzene as a by-product, and the arylchlorosilylene can be isolated in high yields (72% for **30a**, and 93% for **30b**). Both **30a** and **30b** are persistent under the exclusion of air at room temperature. It is notable that the arylchlorogermylene was also synthesized.⁷²

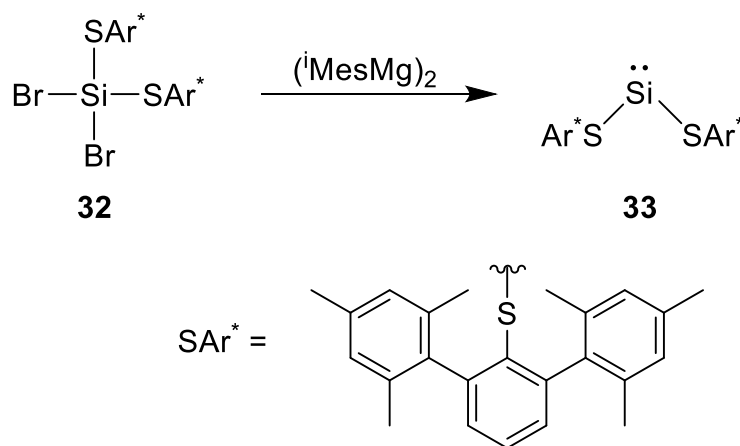


Scheme 23. Synthesis of arylchlorosilylene **30** (Mes = C₆H₂-2,4,6-Me₃, Trip = C₆H₂-2,4,6-^{*i*}Pr₃).

1.3.4 Stable Two-Coordinate Acyclic Silylenes

In contrast to stable cyclic silylenes, the synthesis of stable two-coordinate acyclic silylenes has only recently been achieved. Aldrige and Power independently synthesized the first two-

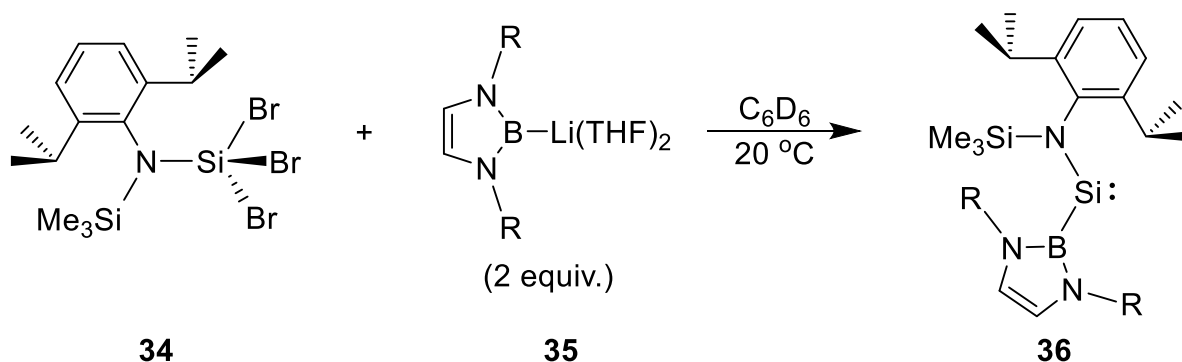
coordinate acyclic silylenes. Power reported the reduction of the silicon(IV) compound, $\text{Br}_2\text{Si}(\text{SAr}^*)_2$ [$\text{Ar}^* = \text{C}_6\text{H}_3-2,6(\text{C}_6\text{H}_2-2,4,6\text{-Me}_3)_2$] (**32**) with $(^i\text{MesMg})_2$ ($^i\text{Mes} = [(2,4,6\text{-trimethylphenyl})\text{NC}(\text{CH}_3)]_2\text{CH}$) gives the silylene, $:\text{Si}(\text{SAr}^*)_2$ (**33**), in 51% yield (Scheme 24).⁷³ The S–Si–S bond angle $[90.519(19)^\circ]$ compares well to that of cyclic silylenes,² but is in sharp contrast to the B–Si–N angle in Aldrige’s acyclic two-coordinate silylene (**36**) $[109.7(1)^\circ]$.⁷⁴ It is notable that while the reaction of **33** with MeI yielded iodomethylbisthiolatosilane, no reaction was observed between compound **33** and hydrogen gas.



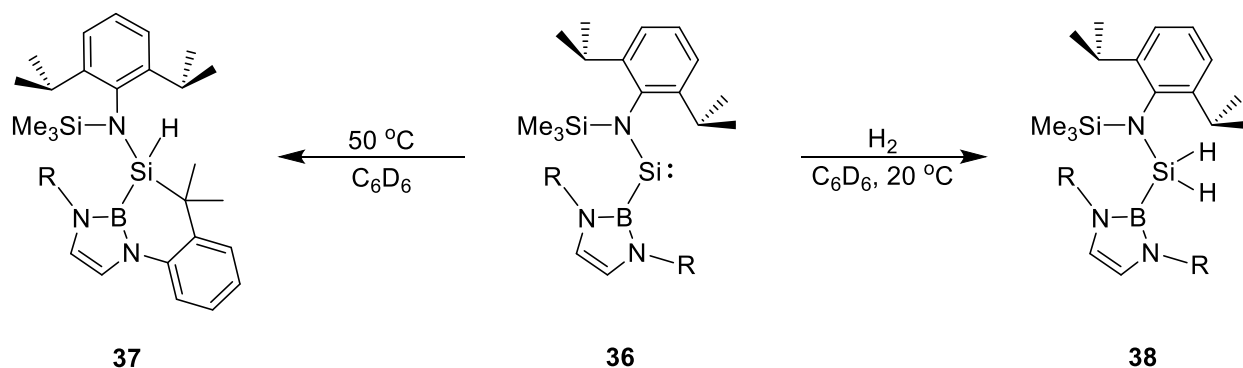
Scheme 24. Synthesis of stable two-coordinate acyclic silylene **33**. ($^i\text{Mes} = [(2,4,6\text{-trimethylphenyl})\text{NC}(\text{CH}_3)]_2\text{CH}$)

Aldrige reported the reaction of an (amido)silicon tribromide, $\text{Si}[\text{N}(\text{SiMe}_3)\text{R}]\text{Br}_3$ (**34**) ($\text{R} = 2,6\text{-diisopropylphenyl}$) with two equivalents of $(\text{THF})_2\text{Li}[\text{B}(\text{NRCH})_2]$ (**35**) to give the corresponding two-coordinate acyclic silylene, $\text{Si}[\text{B}(\text{NRCH})_2][\text{N}(\text{SiMe}_3)\text{R}]$ (**36**) (Scheme 25).⁷⁴ Notably, the boryl unit in **35** plays a critical role in the stabilization of **36**, as reaction of **34** with lithium naphthalenide gives only a disilane. Conversion of **34** to **36** is quantitative by ^1H NMR, implying the formation of the silylene center by reductive elimination. Additionally, the widening of the bond angle at the silylene center [B–Si–N angle, $109.7(1)^\circ$] compared to a cyclic silylene $[\text{Si}(\text{N}^i\text{BuCH})_2, 90.5(10)^\circ]^2$ is indicative of the narrowing of the singlet-triplet gap. Thus, **36** may

have enhanced reactivity when compared with cyclic silylenes. Indeed, at raised temperatures, **36** undergoes intramolecular insertion into the C–H bond on a 2,6-diisopropylphenyl group of the boryl ligand to give compound **37** (Scheme 26). Compound **36** also activates dihydrogen to give the dihydrosilane **38** (Scheme 26). The activation of H₂ and activation of a C–H bond is ascribed largely to the increased reactivity facilitated by the higher angle at the silylene center of **36**. The lower angle silylene center of **33** exhibited no reactivity towards H₂ or C–H bonds.



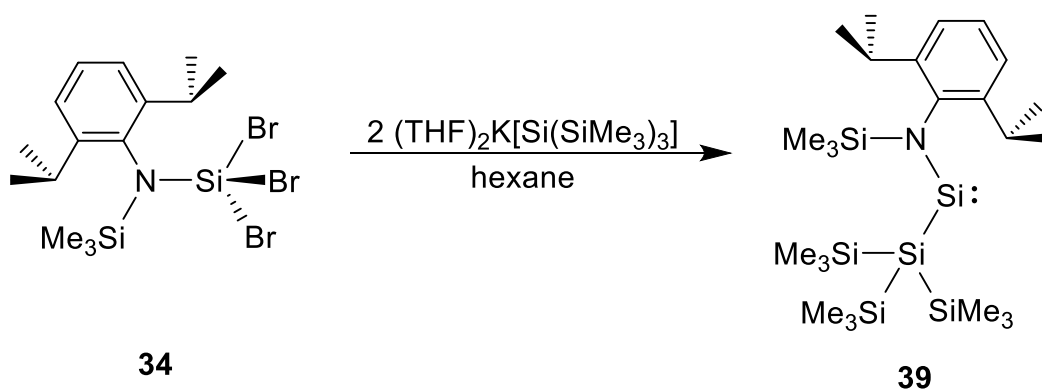
Scheme 25. Synthesis of silylene **36** (R = 2,6-diisopropylphenyl).



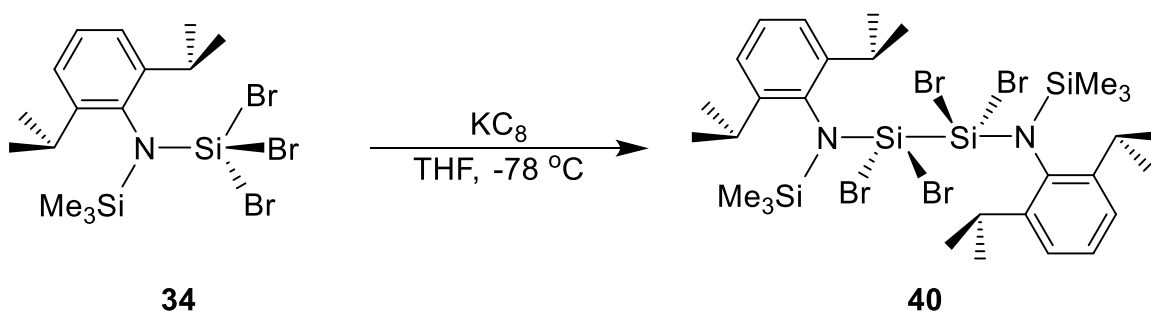
Scheme 26. H₂ and C–H activation by silylene **36** (R = 2,6-diisopropylphenyl).

Subsequently, Aldrige reported that the reaction of **34** with (THF)₂K[Si(SiMe₃)₃] gives the first stable two-coordinate silylsilylene (**39**) (Scheme 27).⁷⁵ Notably, the Si–Si–N angle in **39** [116.91(5)°] is more obtuse than the angle for the acyclic two-coordinate boryl silylene (**36**) (Scheme 27).⁷³ Both the steric bulk and strong reducing capabilities of the anionic reducing agent,

(THF)₂K[Si(SiMe₃)₃], are vital for achieving compound **39**, as the reduction of **34** with potassium graphite only yields the disilane (**40**), and not the desired silylene (Scheme 28). Additionally, substitution chemistry may occur if the reducing agent is not sufficiently sterically bulky. Reaction of **34** with K[CpFe(CO)₂] largely gives the disilane, **40**, though a small amount of the Si–Fe bonded product, [CpFe(CO)]₂(μ-CO)(μ-SiBr[N(SiMe₃)R]) (R = 2,6-diisopropylphenyl), was detected. Similar to compound **36**, compound **39** also activates H₂ and C–H bonds to give the corresponding dihydrosilylene and silaindoline, respectively.



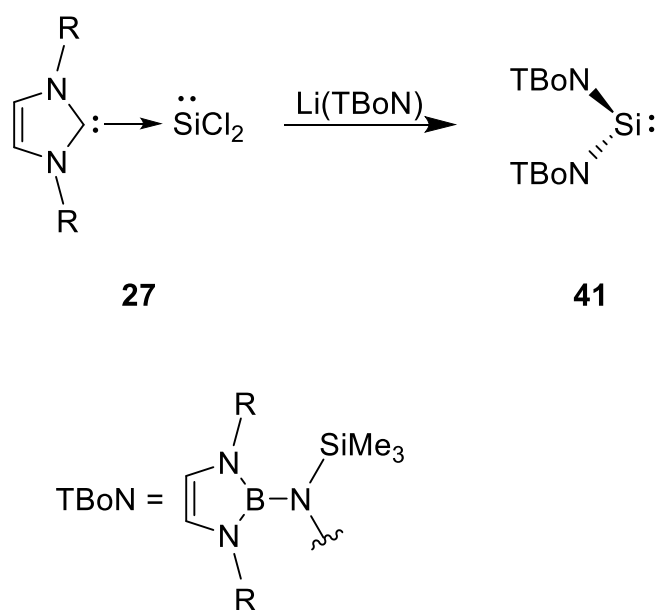
Scheme 27. Synthesis of stable two-coordinate acyclic silylsilylene **39**.



Scheme 28. Synthesis of disilane **40**.

Aldridge reported the synthesis of the first acyclic two-coordinate diaminosilylene in 2016.⁷⁶ Reaction of NHC–SiCl₂ complex (**27**) with Li(TBoN) (TBoN; DAB = [RNCH]₂, R = 2,6-diisopropylphenyl) gives the silylene **41** (Scheme 29). However, compound **41** is formed in a 1:1 ratio with free carbene ligand. The free carbene can be precipitated by addition of either SiBr₄ or

CO₂, neither of which react with compound **41**, and compound **41** can be isolated after removal of NHC-SiBr₄ complex, or NHC-CO₂ complex, respectively. With an N–Si–N angle of 110.94(5)°, the authors predict high reactivity for this silylene, as similarly high angle silylenes such as **36**⁷⁴ or **39**⁷⁵ readily prompt oxidative addition of H₂ and C–H bonds at nearly room temperature, while lower angle silylenes do not.⁷⁶ Additionally, compound **41** participates in the small molecule activation of both O₂ and NH₃, giving a silanone, and a 1:1 mixture of triaminosilane and secondary amine, respectively.⁷⁶

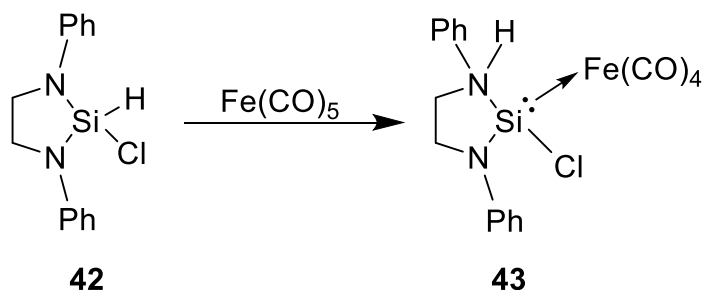


Scheme 29. Synthesis of two-coordinate acyclic diaminosilylene **41** (R = 2,6-diisopropylphenyl).

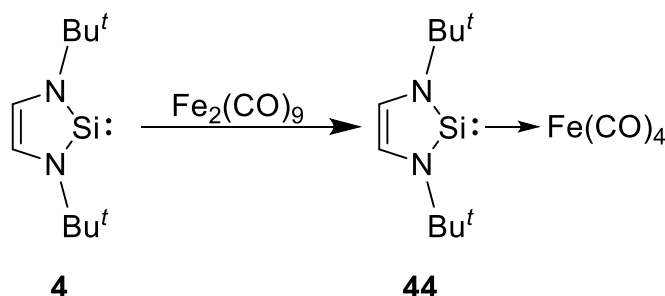
1.3.5 Silylene Transition Metal Complexes

N-heterocyclic silylene-transition metal complexes have been gaining recognition in catalysis.⁵² The first example of an NHSi-iron complex was reported by Welz and Schmid in 1977.⁷⁷ Reaction of 2-chloro-1,3-diphenyl-1,3-diaza-2-silacyclopentane (**42**) with Fe(CO)₅ under photolytic conditions forms the NHSi-Fe(CO)₄ complex (**43**) (Scheme 30). However, the NHSi-Fe(CO)₄ complex is highly thermolabile and decomposes above -20 °C. As such, no structural

characterization was performed.⁷⁷ West synthesized the first stable NHSi-iron complex by reaction of NHSi (**4**) with $\text{Fe}_2(\text{CO})_9$ to yield the NHSi- $\text{Fe}(\text{CO})_4$ complex (**44**) (Scheme 31).⁷⁸

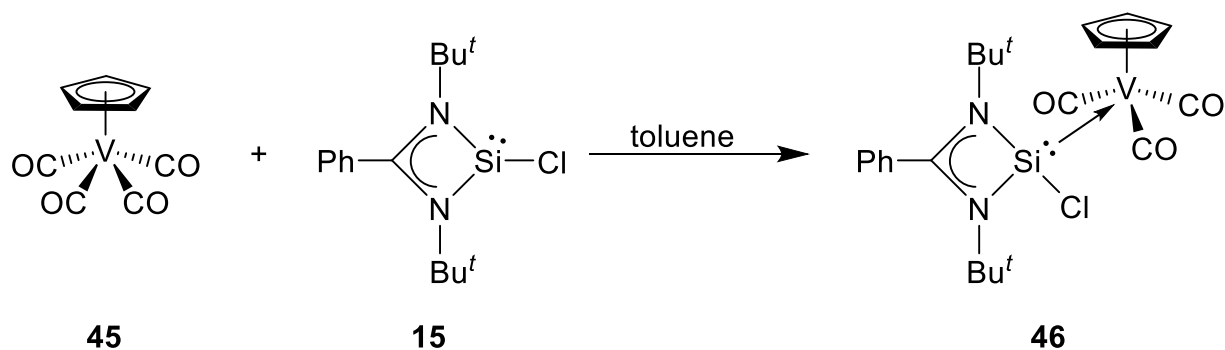


Scheme 30. Synthesis of the first silylene-iron complex **43**.



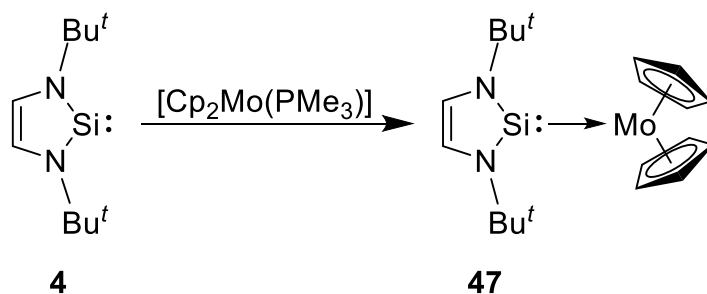
Scheme 31. Synthesis of a silylene-iron complex **44**.

Roesky reported the isolation of an NHSi-vanadium complex, $[\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\mathbf{15})]$ (**46**), by reaction of silylene **15** with $[\text{V}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_4]$ (**45**), giving the NHSi-vanadium complex, through the elimination of one CO ligand (Scheme 32).⁷⁹ The geometry of **46** is that of the typical piano-stool type, with the Cp ring occupying the seat position, and the CO ligands and the silylene in the leg positions of the stool. Interestingly, the Si–V bond length was found to be 2.3866(5) Å, which is markedly shorter than previously reported for vanadium-silyl complexes (2.56 Å),⁸⁰ suggesting some degree of π back-bonding from vanadium to silicon.

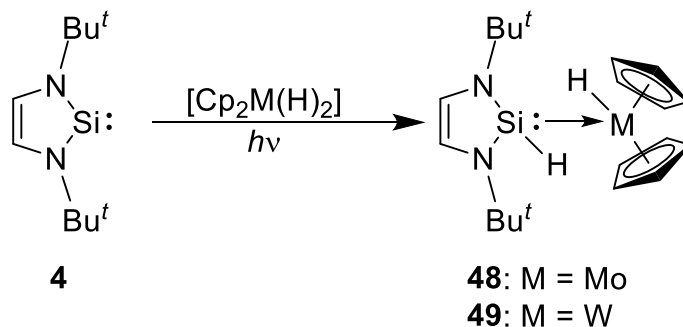


Scheme 32. Synthesis of silylene-vanadium complex **46**.

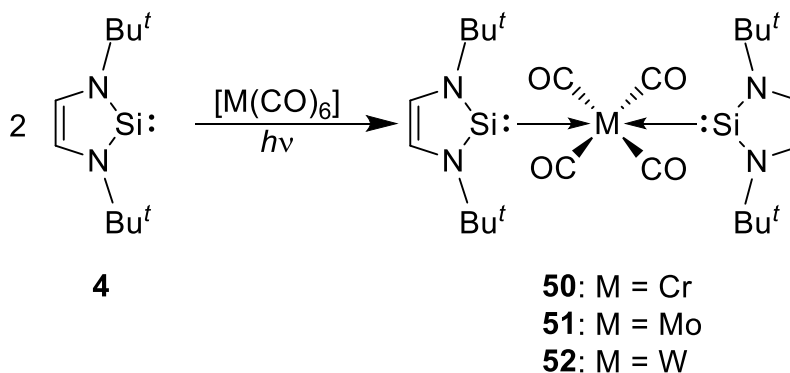
A variety of group 6 transition metal-NHSi complexes have been synthesized. Bradley found that reaction of NHSi (**4**) with phosphorus-stabilized molybdocene [$\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{PMe}_3)$] gave the complex [Cp_2MoNHSi] (**47**) (Scheme 33).⁸¹ Notably, it was reported that reaction of **4** with [Cp_2MH_2] ($\text{M} = \text{Mo}, \text{W}$) under photolytic conditions prompted the insertion of the silicon atom in the M-H bond, giving the hydrosilyl hydrido σ -complexes (**48** and **49**) (Scheme 34).⁸¹ Additionally, irradiation of the $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) in the presence of **4** affords the bis-silylene-metal carbonyl complexes (**50-52**) (Scheme 35).⁷⁸ Roesky reported that the reaction of silylene **15** with [$\text{M}(\text{CO})_5(\text{THF})$] ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) yields the NHSi-metal complexes **53-55** (Scheme 36).⁸² Interestingly, **53-55** can be further treated with trimethyl tin fluoride (Me_3SnF), a fluoride transfer reagent, to give the fluorinated silylene-transition metal complex.



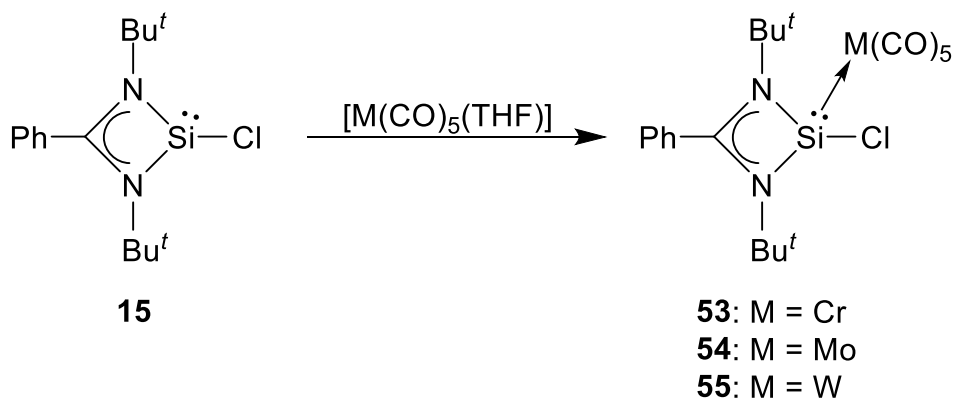
Scheme 33. Synthesis of silylene-molybdenum complex **47**.



Scheme 34. Synthesis of silylene-group 6 transition metal complexes **48** and **49** (M = Mo, W).



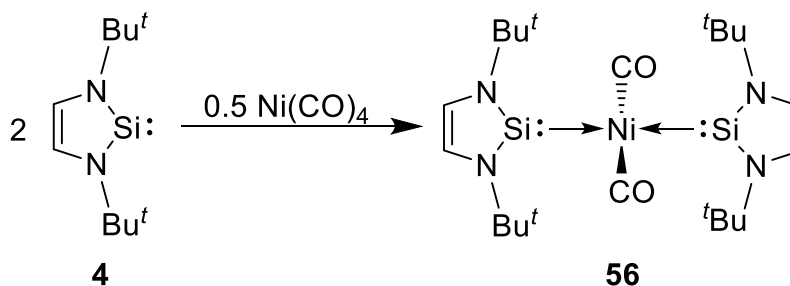
Scheme 35. Synthesis of bis-silylene-group 6 transition metal complexes **50-52** (M = Cr, Mo, W).



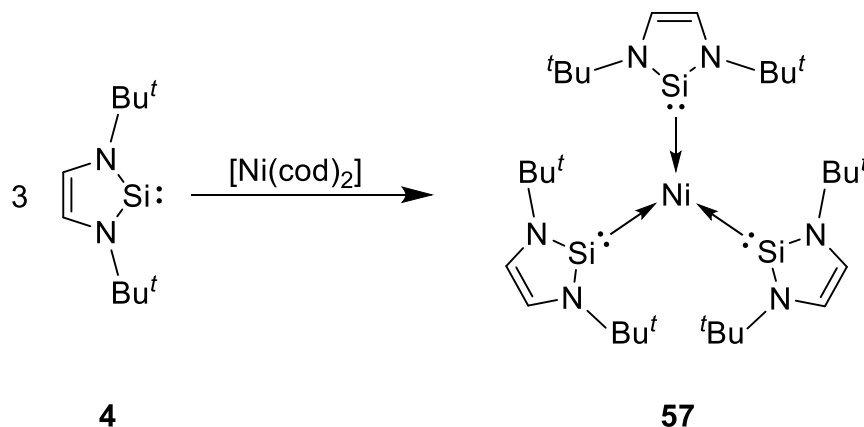
Scheme 36. Synthesis of silylene-group 6 transition metal complexes **53-55** (M = Cr, Mo, W).

The first bis-silylene-Ni(CO)₂ complex (**56**) was synthesized by West through a reaction of silylene **4** with Ni(CO)₄ in a 2:1 ratio [silylene:Ni(CO)₄] (Scheme 37).⁸³ West later reported the

isolation of a trigonal planar tris-silylene-nickel complex (**57**), by combination of three equivalents of compound **4** with one equivalent of $[\text{Ni}(\text{cod})_2]$ (Scheme 38).⁸⁴



Scheme 37. Synthesis of bis-silylene-nickel complex **54**.



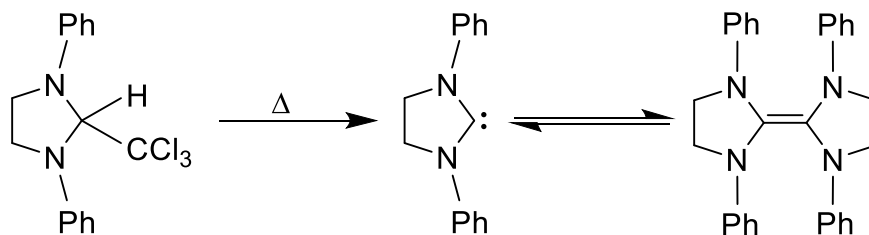
Scheme 38. Synthesis of tris-silylene-nickel complex **55**.

1.4 Stable Carbenes

1.4.1 Historical Perspective

In organic chemistry, the standard valency of carbon was not always recognized, as several carbon compounds were known to exist with carbon in multiple oxidation states ($\text{C}^{\text{II}}\text{O}$, $\text{C}^{\text{IV}}\text{O}_2$, $\text{C}^{\text{I}}\text{H}_4$). Prior to the assertion that carbon primarily exists as a tetravalent species, divalent carbon(II) was hypothesized to exist. The first recorded attempt to isolate divalent methylene ($:\text{CH}_2$) was performed in 1835 by Jean-Baptiste Dumas, through a reaction of methanol with phosphorus

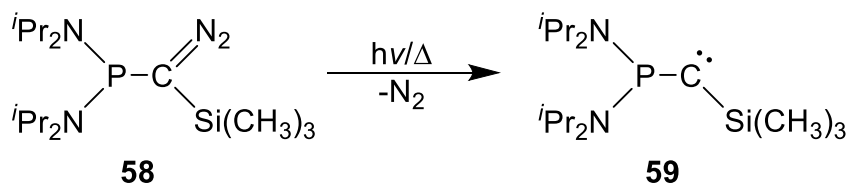
pentoxide or sulfuric acid.⁸⁵ However, Dumas only isolated diethyl ether. In 1862, Anton Geuther proposed that the dehydrohalogenation of chloroform with potassium ethoxide yielded the dichlorocarbene, :CCl_2 .⁸⁶ However, this species is highly reactive, and Geuther did not isolate a product. Helmut Scheibler predicted that the reaction of sodium ethoxide with esters would give tetraethoxyethylene, which could then decompose into diethoxycarbene $[\text{:C}(\text{OCH}_3)]$, but no products were isolated.⁸⁷ The next investigation into potential carbene chemistry was performed by Martin Schmeisser in 1960.⁸⁸ Schmeisser postulated that reaction of tetrachloromethane with activated carbon at extremely high temperatures (1300°C) would give the desired dichlorocarbene, but the only isolated products were dichloroacetylene and chlorine gas. Hans-Werner Wanzlick, who was a former student of Scheibler's, proposed an equilibrium between a free carbene and its dimer, by elimination of chloroform from 1,3-diphenyl-2-trichloromethylimidazolidine (Scheme 39).⁸⁹ He found that addition of ancillary amino groups could help stabilize a carbene center.⁸⁹ However, the existence of this equilibrium was disproven by David Lemal in 1964, who showed that Wanzlick only isolated the dimer.⁹⁰ In 1970, Wanzlick proposed the formation of free carbene by deprotonation of an imidazolium salt, but unfortunately never attempted to isolate the free product.⁹¹ Instead, the carbene was generated *in situ* in order to coordinate several transition metal species.⁹²



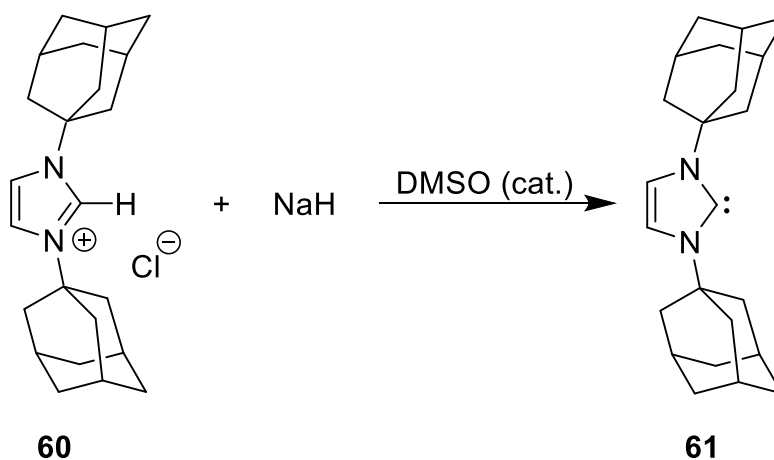
Scheme 39. Proposed equilibrium between an N-heterocyclic carbene and the dimer.

Dismissed as highly reactive intermediates, investigation into carbenes declined for almost two decades. The long sought-after discovery of the first stable carbene came from Guy Bertrand

in 1988.⁹³ Reaction of the lithium salt of (trimethylsilyl)diazomethane with bis(diisopropylamino)chlorophosphine gives (trimethylsilyl)-[bis(diisopropylamino)phosphino]-diazomethane (**58**) (Scheme 40). Thermolysis or photolysis of **58** yielded the first stable carbene, [bis(diisopropylamino)phosphino]trimethylsilylcarbene (**59**), which was stable at room temperature under inert atmosphere (Scheme 40). However, carbenes were still considered, in Bertrand's own words, 'chemical curiosities,'⁹⁴ and were dismissed as such. The keystone discovery in carbene chemistry came in 1991, when Anthony Arduengo synthesized the first 'bottleable' stable crystalline carbene.⁵ Deprotonation of 1,3-di-1-adamantylimidazolium chloride (**60**) with potassium hydride or sodium hydride with a catalytic amount of potassium *tert*-butoxide or dimethyl sulfoxide anion gives the free carbene (**61**) in nearly quantitative yield (Scheme 41).⁵

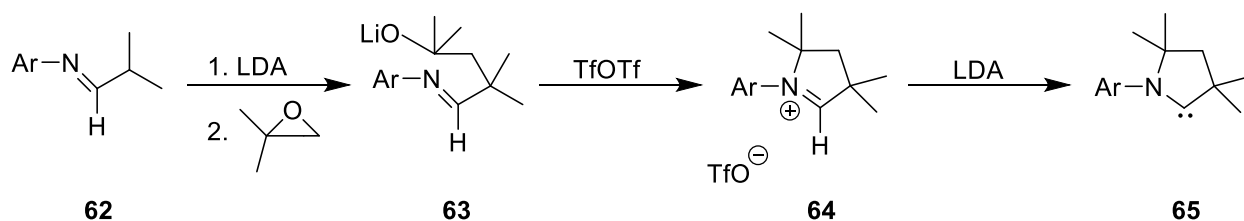


Scheme 40. Synthesis of the first stable carbene (**59**).

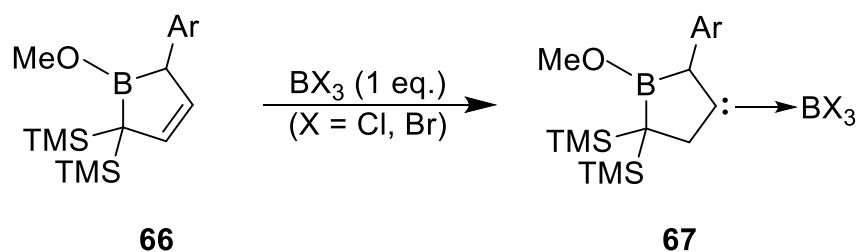


Scheme 41. Synthesis of the first stable crystalline carbene (**61**).

While Arduengo's NHC revolutionized the field of carbene chemistry, it certainly wasn't the only milestone discovery. Developed by Bertrand in 2005, cyclic(alkyl)(amino)carbenes (CAACs) have received significant attention.^{10, 95-98} Rather than two nitrogen atoms α to the carbene center as in NHCs, CAACs contain only one nitrogen atom adjacent to the carbene center. Deprotonation of the corresponding cyclic iminium salt (**64**) gives the CAAC (**65**) (Scheme 42). It is noteworthy that Kinjo recently reported the formation of a CAAC-BX₃ complex (**67**) (X = Cl, Br) from a 1,2-azaborole derivative (**66**) through a 1,2-hydrogen migration (Scheme 43).¹² However, the free 1,2-azaborole-derived CAAC ligand has not yet been achieved.



Scheme 42. Synthesis of CAAC **65**.



Scheme 43. Synthesis of a CAAC-BX₃ complex (**67**).

1.4.2 Electronic Structure of NHCs

In contrast to the parent silylene (:SiH₂, in the singlet ground state), the parent carbene (:CH₂) is much more reactive, due to its triplet ground state.⁹⁹ The triplet carbene exists as a diradical, with each unpaired electron occupying orthogonal 2p orbitals (Figure 6). However, there

are few reports of stabilized triplet carbenes,^{94, 100} and singlet carbenes dominate reported carbene chemistry.

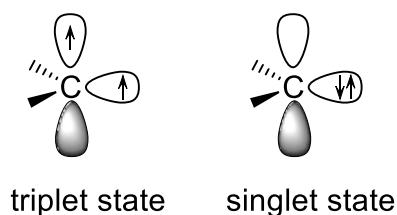


Figure 6. Triplet and singlet state carbenes.

N-heterocyclic carbenes exist as singlet carbenes. The electronic properties of the nitrogen atom(s) promote stability of the carbene, and are considered to play a pivotal role in stabilizing the carbene center.⁶ The nitrogen atoms in a classical NHC act as both σ -electron withdrawing groups, and π -electron donating groups. The σ -electron withdrawing nitrogen atoms lower the energy of the σ orbital of the carbene carbon, while simultaneously delivering π -electron density to the empty p orbital of the carbene carbon. This “push-pull” electronic mechanism provides overall stability to NHCs (Figure 7).^{6, 88, 94, 101}

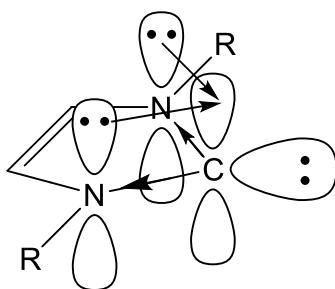


Figure 7. “Push-pull” electronic stabilization of NHCs.

In addition to the predominant electronic effects, steric effects also play an important role in stabilizing NHCs.⁶ For divalent carbon, there are two bonding geometries, linear, and bent. When the structure is bent, this breaks the degeneracy in the nonbonding p orbitals.⁷ As the angle at the carbene center is reduced, one of these p orbitals begins to hybridize into an sp^2 orbital, which elevates the energy level of the LUMO, thus giving a predominantly singlet ground state

for a bent carbene.¹⁰² It is important to note that Bender and Schaefer computed that the triplet ground state of methylene is not linear, but bent.¹⁰³ Additionally, sterically demanding ancillary groups on the nitrogen atom(s) provide a measure of stability for the NHC, as they prevent dimerization.¹⁰²

In the case of unsaturated NHCs, aromaticity can bolster the relative stability of the carbene through the aromatic stabilization energy effect. Indeed, for the unsaturated model imidazol-2-ylidenes, partial aromaticity contributes 20-25 kcal/mol towards stability of the NHC when compared to saturated NHCs. This can allow for smaller ancillary groups on the nitrogen atoms such as methyl or isopropyl groups, since the loss in steric stability is compensated by the increased stability from the partial aromaticity.^{6, 102}

1.4.3 Electronic Properties of CAACs

While classical NHCs have two σ -electron withdrawing and π -electron donating nitrogen atoms in the heterocycle, CAACs have only one, with a nitrogen replaced by a σ -donating carbon atom. This gives CAACs a higher energy HOMO than NHCs, as well as a lower energy LUMO, leading to a larger HOMO-LUMO gap for CAACs when compared with NHCs. Indeed, there is a 93 kJ mol⁻¹ difference in the singlet-triplet energies of a simplified NHC (**a**, Figure 8) and a simplified CAAC (**b**, Figure 8), making CAACs both better σ -electron donors and π -electron acceptors than NHCs. CAACs are not only more nucleophilic but also more electrophilic than NHCs. Thus, CAACs bond to substituents more tightly than NHCs.^{95, 98}

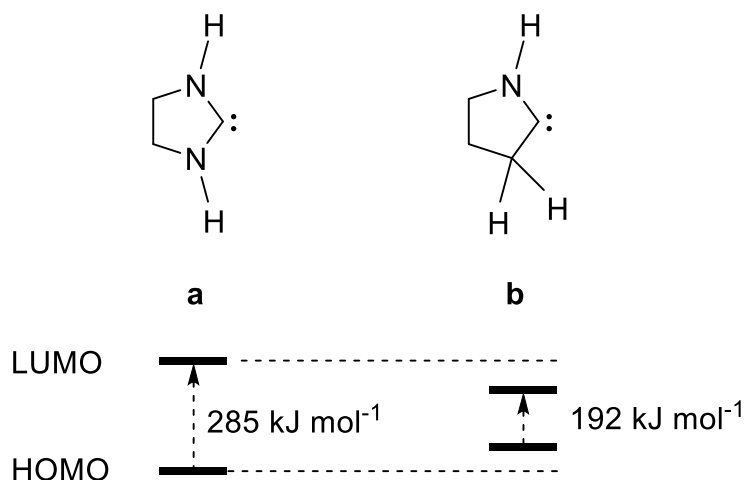
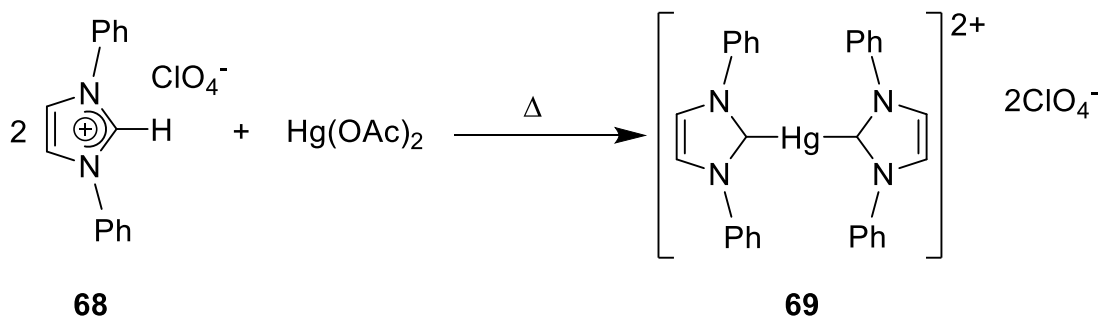


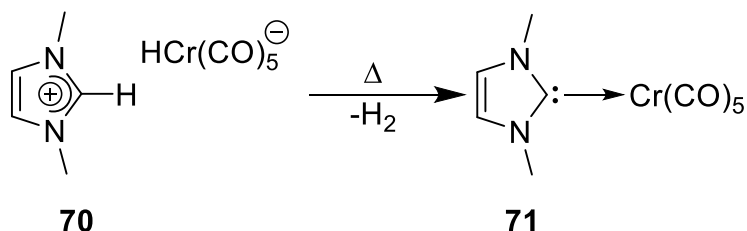
Figure 8. Comparison of the calculated singlet-triplet gap for NHC (**a**), and CAAC (**b**).

1.4.4 Carbene Complexes of Transition Metal and Main Group Species

Both NHCs and CAACs can coordinate to transition metal and main group species. In fact, the first examples of NHC-transition metal complexes appear some 20 years before the isolation of the first stable carbene. Wanzlick and Öfele reported NHC-mercury(0) (**69**)⁹² (Scheme 44) and NHC-chromium(II) adducts (**71**)¹⁰⁴ (Scheme 45), respectively, in 1968. NHCs possess excellent σ -donor capabilities and can donate the carbon-based lone pair of electrons to an empty orbital of a transition metal. Gernot Frenking calculated that π -electron back-donation to the empty p-orbital of the carbene carbon can account for 20% of the bonding energy in group 11-NHC complexes.¹⁰² NHC-transition metal chemistry is pervasive, with applications in materials,⁶ pharmaceuticals,¹⁰⁵ and as organocatalysts.⁸



Scheme 44. Synthesis of a carbene-mercury complex (69).



Scheme 45. Synthesis of a carbene-chromium complex (71).

While many NHC-transition metal complexes are well-known, NHC-stabilized low-oxidation-state-main group complexes are gaining substantial attention.⁹ As with transition metal complexes, NHCs can donate the carbon-based lone pair of electrons to a vacant orbital, most commonly an empty p-orbital for main group species. The dative bond from the carbene center to the main group moiety is a robust interaction, and the majority of these NHC-main group complexes possess high stability and are non-labile.⁸⁸ This high stability allows for further reactivity on the main group species without dissociation from the carbene. The strong interaction between the carbene carbon and the main group moiety has allowed a number of highly reactive main group species to be stabilized.⁹

1.5 Conclusion

Silicon is an essential element in the modern world. It is unrivaled as a semiconductor, and some silicon compounds are gaining recognition as metal-free catalysts. Though silicon and carbon

are adjacent group 14 elements, their properties and reactivity vary dramatically. Through several key discoveries, modern organosilicon chemistry has made progressive strides over the previous 80 years.

Advances in organosilicon chemistry have provided chemists with new methods to access multiply bonded silicon compounds. However, synthesis of low valent silicon compounds has proven to be an increasingly difficult topic when compared with the synthesis of low valent carbon compounds. Indeed, the first Si=Si double bond was isolated in 1981, and the first Si≡Si triple bond was isolated in 2004, emphasizing the difficulty in synthesizing novel low valent silicon compounds.

As an extension of the work on multiply bonded silicon, the chemistry of silylenes ($:\text{SiR}_2$) is still in development. Silylenes offer a Lewis basic silicon platform from which to access novel silicon-based compounds. N-heterocyclic silylenes are particularly stable, as the nitrogen atoms in the heterocycle provide additional stability to the silylene. Silylenes are seeing use in the coordination of transition metals and in small molecule activation. Acyclic silylenes have also been recently developed and are valuable in the activation of several small molecules (O_2 , H_2 , NH_3) as well as in the activation of C–H bonds.

Since the synthesis of the first stable, crystalline N-heterocyclic carbene, carbenes have been utilized in numerous applications, including catalysis, transition metal coordination, and the stabilization of highly reactive main group species. In addition to classical NHCs, the cyclic (alkyl)(amino)carbenes, developed by Bertrand, have seen similar utility. As better σ -donors and π -acceptors than NHCs, CAACs can stabilize highly reactive species not accessible through NHC stabilization. Despite the extensive utility of NHCs and CAACs, developing novel carbene systems still fascinates chemists. Interestingly, computations show that Kinjo's CAAC is even more

nucleophilic and electrophilic than Bertrand's CAAC, since it has a lower LUMO and higher HOMO. More recently, work on the synthesis of 1,2-azaborole-derived CAAC complexes of boron trihalides has shown that there is still much to discover in intriguing carbene chemistry. This research project involves silylene-transition metal coordination, cyclic silylenes, and group 13 Lewis acid-induced diazaborole-derived carbene complexes of boron.

CHAPTER 2

RESULTS AND DISCUSSIONS

2.1 Transition-Metal-Mediated Cleavage of a Si=Si Double Bond

The chemistry of disilenes has been widely developed since the first reported synthesis by Robert West in 1981.^{32-33, 106-113} Indeed, disilenes have been utilized to coordinate transition metal complexes, where the transition metal is coordinated to the disilene in a η^2 -fashion.^{111, 114-126} Based on the Dewar-Chatt-Duncanson model, disilene-transition metal complexes are generally categorized as either π -complexes (**a**) or metallacycles (**b**) (Figure 9).^{111, 127} Recently, an η^1 -disilenide zirconium complex was shown to isomerize to give a cyclic silyl complex through a 1,2-addition of a methyl C–H bond to the Si=Si double bond.¹²⁸ While cleavage of silicon-silicon double bonds by main group or organic species in disilene-transition metal complexes has been reported,^{107, 115, 124} the direct cleavage of a Si=Si double bond by a transition metal compound had not been previously been achieved.

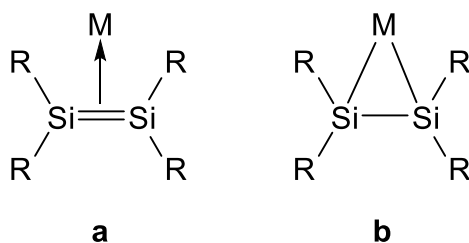


Figure 9. The Dewar-Chatt-Duncanson model of transition metals with disilenes: **a**) disilene-transition metal π -complex; **b**) disilene-transition metal metallacycle.

Transition metal complexes of silylenes,^{4, 52, 77, 122, 129-132} the silicon analog of carbenes, are showing promise in catalysis.^{52, 132} Though there are many examples of silylenes and disilenes in the literature, there are only a handful of compounds containing both a Si=Si double bond and a

silicon-based electron lone pair (disilenides **I**),¹³³⁻¹³⁷ carbene-disilyne complex **II**,¹³⁸ carbene-coordinated disilenyl silylene **III**,¹³⁹ carbene-stabilized disilicon(0) **IV**,³⁶ Figure 10). Interestingly, the carbene-disilyne complex (**II**) has been reported to act as a σ -donor to coordinate ZnCl_2 .¹³⁸ This laboratory reported the fluxional behavior of a CuCl species about the Si_2 core of carbene-stabilized disilicon(0), with interconversion between the σ and π bonding modes.¹⁴⁰ Remarkably, in the solid state, only the σ -coordination mode was observed. The carbene-stabilized $[\text{L}:\text{GeFe}(\text{CO})_4]_2$ cluster contains both σ - and π -type coordination of the $\text{Fe}(\text{CO})_4$ unit.¹⁴¹ These promising finds led us to investigate the reactivity of iron carbonyl with carbene-stabilized disilicon(0). Herein, we report the syntheses, structures, and computations of carbene-stabilized $\text{Si}_2\text{Fe}(\text{CO})_4$ (**72**) and $\text{Si}[\mu\text{-Fe}_2(\text{CO})_6](\mu\text{-CO})\text{Si}$ (**73**). Compound **73** represents the first example of transition-metal-mediated cleavage of a $\text{Si}=\text{Si}$ double bond.

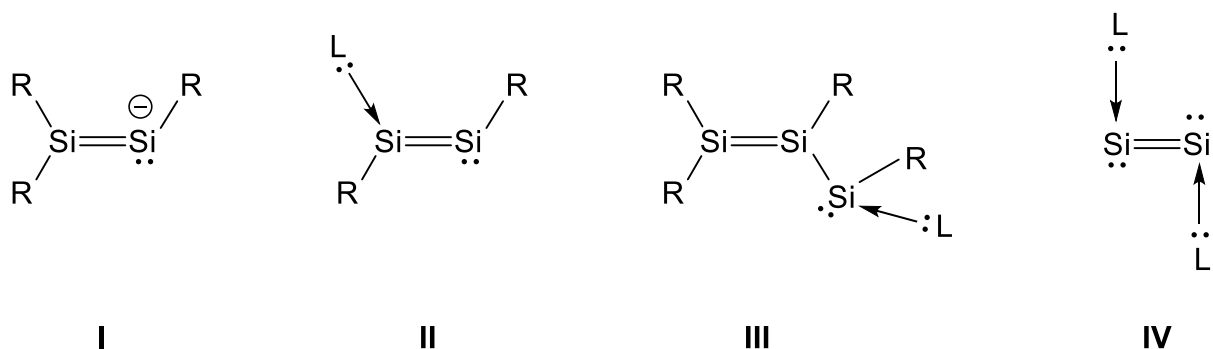
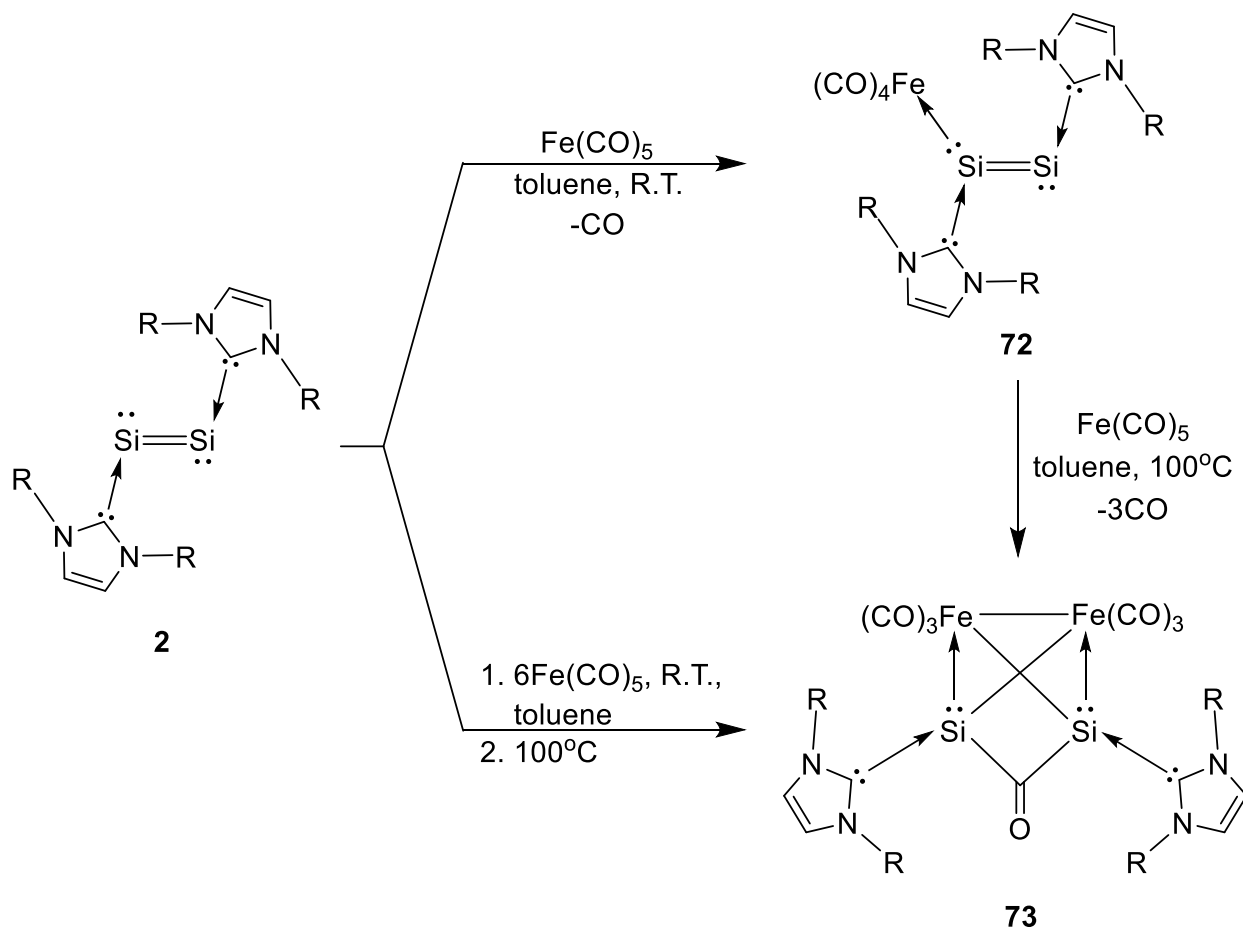


Figure 10. Compounds containing both a $\text{Si}=\text{Si}$ double bond and a silicon-based lone pair.

Reaction of $\text{Fe}(\text{CO})_5$ (yellow) with carbene-stabilized disilicon(0) (**2**) (dark red) in toluene in a 1:1 ratio affords the $\text{Fe}(\text{CO})_4$ -disilicon complex (**72**) (dark purple) in high yield (81%) (Scheme 46). Reaction of excess $\text{Fe}(\text{CO})_5$ with **2** at room temperature only gives the 1:1 complex product. Reaction of the $\text{Fe}(\text{CO})_4$ -disilicon complex (**72**) with an additional equivalent of $\text{Fe}(\text{CO})_5$ (1:1) in toluene, heated overnight at 100°C , affords **73** in 97% yield as an orange crystalline solid (Scheme 46). Heating of compound **72** in the absence of $\text{Fe}(\text{CO})_5$ simply results in decomposition

of the $\text{Fe}(\text{CO})_4$ -disilicon complex. Additionally, compound **72** shows no reactivity with CO gas, suggesting the importance of the second equivalent of $\text{Fe}(\text{CO})_5$ in the formation of **73**. Compound **73** may also be synthesized directly by reaction of **2** with excess $\text{Fe}(\text{CO})_5$ at room temperature overnight, followed by reaction overnight at 100°C . However, this method lowers the yield significantly (42%). It is of note that a $\text{NHC-Fe}(\text{CO})_4$ complex was isolated as a biproduct during the direct formation of **73**.



Scheme 46. Synthesis of compounds **72** and **73**.

The X-ray structure of **72** reveals that one of the silicon-based lone pairs acts as a σ -donor to coordinate one $\text{Fe}(\text{CO})_4$ (Figure 11). Large steric repulsion between the carbene ligands and the $\text{Fe}(\text{CO})_4$ unit likely prevents the formation of the 2:1 product. It is noteworthy that the 2:1 complex

product has been isolated in a $[L'Ge[Fe(CO)_4]]_2$ complex, where the carbene ligand is significantly less bulky ($L' = :C[(Pr^i)NC(Me)]_2$).¹⁴¹ The Si–Fe bond in **72** [2.3265(10) Å] is slightly longer than the Si–Fe bond in the computed $Fe(CO)_4$ -disilicon complex (**72-Me**) (2.364 Å) and for $H_2Si[Fe(CO)_4]$ (2.41 Å),¹⁴² and is longer than those reported for $Fe(CO)_4$ -silylene complexes (2.196–2.294 Å).^{78, 143} The short Si–Fe bond in $NHSi:Fe(CO)_4$ (2.196 Å) ($NHSi: = :Si[(t-Bu)NCH]_2$) is attributed to iron-silicon π -backbonding.⁷⁸ The Si=Si double bond [2.1951(12) Å] and the Si–C bonds (1.941 Å, av.) in **72** are comparable to those in **2** [$d_{Si=Si} = 2.2294(11)$ Å; $d_{Si-C} = 1.9271(15)$ Å, av.], **72-Me** [$d_{Si=Si} = 2.215$ Å; $d_{Si-C} = 1.954$ Å, av.], and in **74** [$d_{Si=Si} = 2.2061(12)$ Å; $d_{Si-C} = 1.928$ Å, av.] (Figure 14). In contrast with **74** (singlet, 226.7 ppm in C_6D_6), **72** exhibits two separate singlets in the ^{29}Si NMR spectrum (201.3 and 142.5 ppm in $[D_8]THF$), suggesting that the asymmetric structure found in the solid state of **72** exists in solution as well. The lack of fluxional behavior of the $Fe(CO)_4$ unit around the Si_2 core is likely due to the large steric bulk of $Fe(CO)_4$ compared to the smaller $CuCl$ in compound **74**. Additionally, the ^{13}C NMR resonance of the terminal carbonyl in compound **72** (218.7 ppm) is comparable to that of compound **73** (221.1 ppm) and in $L:SiCl_2[Fe(CO)_4]$ (215.0 ppm) ($L: = C\{N(2,6-Pr^i_2C_6H_3)CH\}_2$).¹⁴⁴

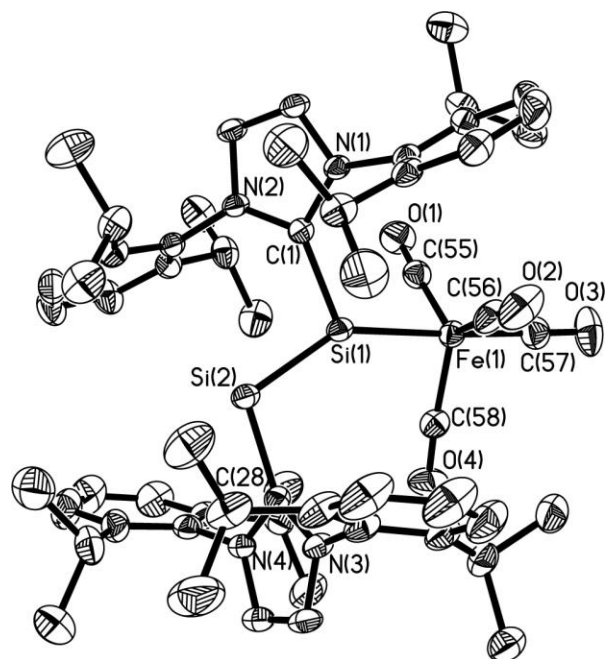


Figure 11. Molecular structure of **72**. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Si(1)–Si(2) 2.1951(12), Si(1)–C(1) 1.942(3), Si(2)–C(28) 1.940(3), Si(1)–Fe(1) 2.3265(10), Fe(1)–C(57) 1.753(4); C(1)–Si(1)–Si(2) 101.66(9), Si(1)–Si(2)–C(28) 106.54, Si(2)–Si(1)–Fe(1) 144.41(5), C(1)–Si(1)–Fe(1) 113.40(9).

DFT computations were performed at the B3LYP/6-311 +G** level on a simplified model of **72** (**72-Me**) (optimized in C_1 symmetry). While the Si–Cu bond in the simplified CuCl–disilicon complex (**74-Me**) is highly polarized towards silicon (78%), natural bond order (NBO) calculations show that the Si–Fe bond in **72-Me** [Wiberg bond index (WBI) = 0.69] is polarized only slightly towards silicon (51%). The Si=Si double bond in **72-Me** has a WBI of 1.75, which compares well to the Si=Si double bond in the simplified carbene-stabilized disilicon(0) model (**2-Ph**) (1.73), as well as the Si=Si double bond in **74-Me** (1.63), which suggests that **72** contains a Si=Si double bond. The Si–Si σ -bonding orbital in **72-Me** involves the overlap of the approximately sp^2 hybridized Si(1) atomic orbital (35.9% s, 63.9% p, 0.2 % d) with the Si(2)

atomic orbital that is principally p character (16.8% s, 82.7% p, 0.5% d). Additionally, the Si–Si π -bonding orbital is almost entirely p character (98.7%) (Figure 12).

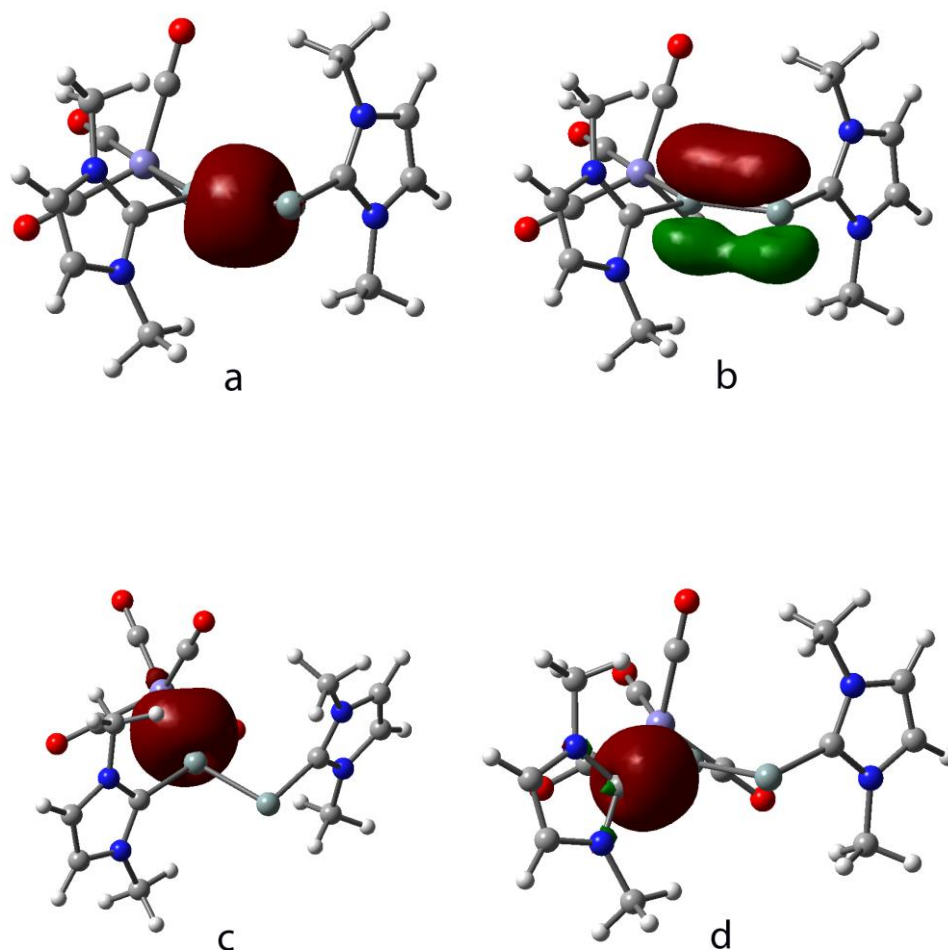


Figure 12. Selected Natural bond orbitals of **72-Me**. a) Si–Si σ -bonding orbital; b) Si–Si π -bonding orbital; c) Si–Fe σ -bonding orbital; d) Si–C σ -bonding orbital

The X-ray crystal structure of **73** reveals that one equivalent of $\text{Fe}(\text{CO})_5$ may react with one equivalent of **72** at high temperatures to cleave the Si=Si double bond and insert CO and $\text{Fe}_2(\text{CO})_6$ units between the two L:Si: components ($\text{L} = \text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}\}_2$). Indeed, there are few examples of reactivity between CO and silicon compounds.¹⁴⁵⁻¹⁴⁸ Scheschkewitz *et al.* have reported the direct carbonylation of cyclotrisilenes with CO.¹⁴⁵ Sekiguchi and coworkers realized a disilyl ketone through CO insertion into the strained silicon-silicon bond of silyl-

substituted 1,4-disila.¹⁴⁶ Moreover, silylene-CO complexes have only been observed in hydrocarbon matrices at 77 K.¹⁴⁷ Synthesis of Sekiguchi's disilyl ketone was proposed to involve a biradical intermediate, but the relative mechanism of **73** is still unknown. The Si(1)–C(29) and Si(2)–C(29) bond distances [1.957(3) and 1.937(4) Å] are slightly shorter than those for the C=O group in the disilyl ketone [1.9730(17) and 1.9807(16) Å]. The ¹³C (247.5 ppm) and IR stretching band (1628 cm⁻¹) for the bridging CO in **73** compare well to those for the disilyl ketone (260.3 ppm and 1673 cm⁻¹, respectively). The calculated IR absorption (1636 cm⁻¹) of the bridging CO in the simplified model of **73** (**73-Me**) (optimized in C₂ symmetry) is close to that observed experimentally for **73**. The silicon-silicon distance in **73** is 2.5206 Å, which is longer than the sum of the silicon covalent radii (2.34 Å).¹⁴⁹ Both silicon atoms in **73** share three electrons with the Fe₂(CO)₆ unit: two electrons through a Si–Fe donor-acceptor bond, and one electron through a Si–Fe covalent bond. The Si–Fe bonds [2.2867(8) and 2.2930(8) Å] compare well to the computational values, as well as reported bond distances for silylene-Fe(CO)₄ complexes [2.196–2.294 Å].^{78, 143} The Si–Fe bonds in **73** are obviously shorter than those in reported iron-silyl bonds (2.493 Å, av) in *cis*-[Fe(xantsil)(CO)₄].¹⁵⁰ Accounting for the valence electrons contributed by the carbene ligands, the Si[μ-Fe₂(CO)₆](μ-CO)Si core in **73** is isoelectronic to the inorganic core in RP[μ-Fe₂(CO)₆](μ-CO)PR¹⁵¹ (compound **75**, Figure 15) [R = N(Pr^{*i*})₂] and S[μ-Fe₂(CO)₆](μ-CO)S (compound **76**, Figure 15).¹⁵² The Fe–Fe bond length in **73** [2.6658(8) Å] compares well to the computed value in **73-Me** (2.739 Å). The Fe–Fe bond distance decreases from **73** [2.6658(8) Å], to the phosphorus analog **75** [2.603(2) Å], to the sulfur analog **76** [2.488(1) Å], corresponding to the blue shift for the bridging C=O in **73**, **75**, and **76** (1628, 1720, 1775 cm⁻¹), respectively.

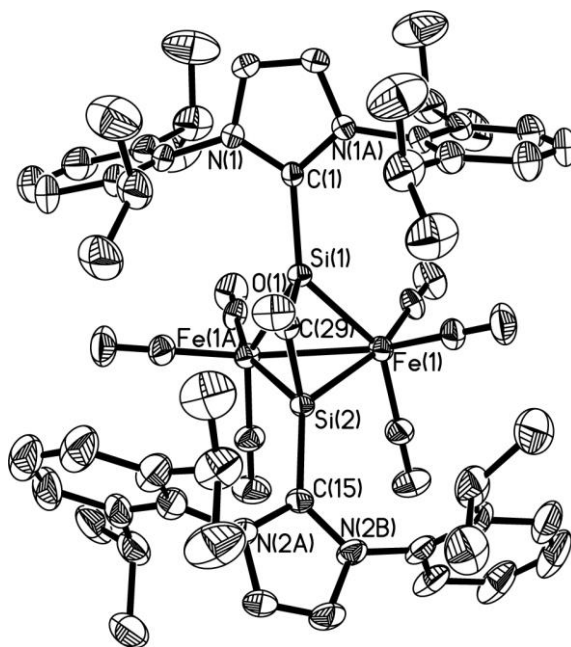


Figure 13. Molecular structure of **73**. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Si(1)...Si(2) 2.5206(13), Si(1)–C(1) 1.933(3), Si(2)–C(15) 1.935(3), C(29)–O(1) 1.194(4), Si(1)–C(29) 1.957(3), Si(2)–C(29) 1.937(4), Si(1)–Fe(1) 2.2867(8), Si(2)–Fe(1) 2.2930(8), Fe(1)–Fe(1A) 2.6658(8); C(1)–Si(1)–Fe(1) 134.11(6), C(1)–Si(1)–C(29) 114.21(15), Si(1)–C(29)–Si(2) 80.67(14), Si(1)–Fe(1)–Si(2) 66.79(3), Si(1)–Fe(1)–Fe(1A) 54.34(2).

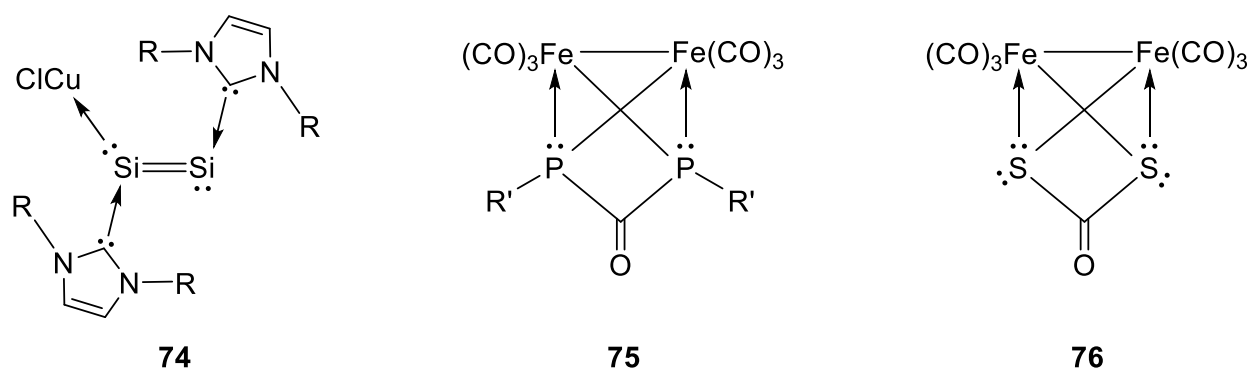


Figure 14. Relevant compounds **74**, **75**, and **76** ($R' = N(iPr)_2$).

NBO analysis shows the Si–Fe bonds in **73-Me** are polarized slightly towards iron (53.3% and 56.4%) (Figure 15). The WBI (0.63-0.68) of the Si–Fe bonds in **73-Me** are close to that for

72-Me (0.69). Additionally, the WBI of the Fe–Fe single bonds in **73** (0.36) is consistent with those (0.34–0.35) of the Fe–Fe single bonds in singlet binuclear iron carbonyl complexes [*i.e.*, $(\text{C}_5\text{F}_6)\text{Fe}_2(\text{CO})_7$].¹⁵³

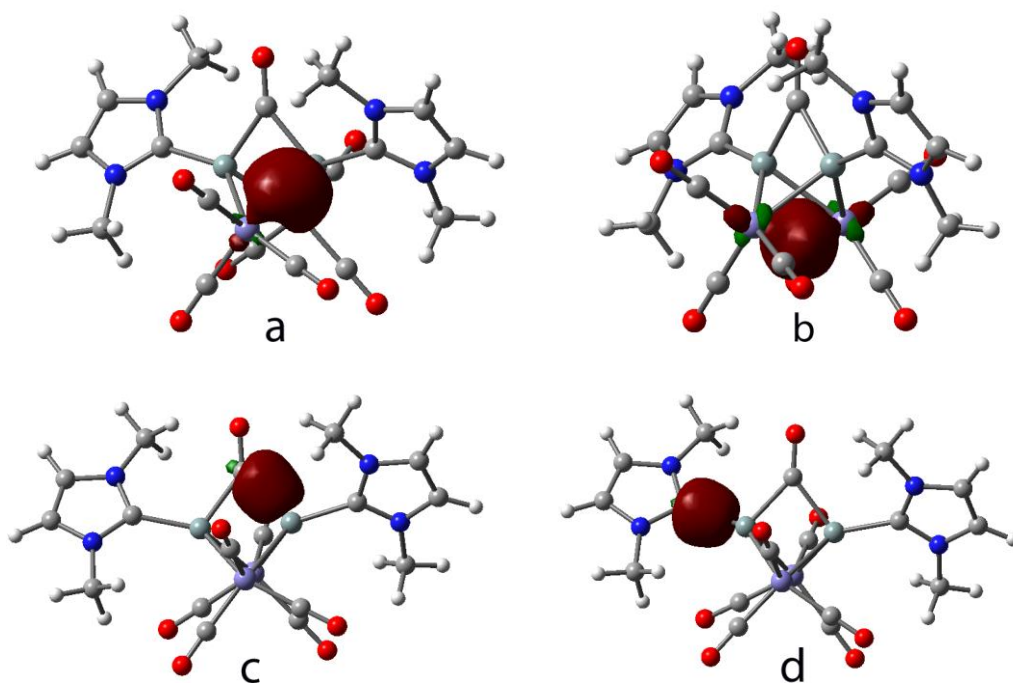


Figure 15. Selected Natural bond orbitals of **73-Me**. a) Si–Fe σ -bonding orbital; b) Fe–Fe σ -bonding orbital; c) Si–C_{bridging} σ -bonding orbital; d) Si–C_{NHC} σ -bonding orbital.

Reaction of **2** with one equivalent of iron pentacarbonyl at room temperature affords the disilicon-Fe(CO)₄ complex, **72**. Treatment of **72** with an additional equivalent of iron pentacarbonyl at raised temperatures affords compound **73**, inserting both CO and Fe₂(CO)₆ units between the two L:Si fragments, cleaving the Si=Si double bond. Alternatively, **73** may be prepared directly by reaction of **2** with excess iron pentacarbonyl overnight at room temperature, followed by an additional overnight reaction at raised temperatures. Notably, compound **73** represents the first example of direct Si=Si double bond cleavage by a transition metal species.

2.2 Push-Pull Stabilization of a Parent Monochlorosilylene

Since the first observation of silylenes ($:\text{SiR}_2$),¹⁵⁴ the silicon analog of carbenes, interest in these fleeting divalent silicon species has increased dramatically.^{107, 154-159} Since the synthesis of stable silylenes such as $:\text{Si}(\eta^5\text{-C}_5\text{Me}_5)_2$ and $:\text{Si}[\text{N}(\text{tBu})\text{-CH}]_2$,^{2, 47, 157} silylenes have seen utilization in the synthesis of transition metal complexes.^{4, 52, 77, 122, 129-132, 143, 160-168} In addition to their ability to coordinate transition metal species, silylenes are receiving attention for their catalytic properties.^{52, 132} The parent silylene ($:\text{SiH}_2$)¹⁶⁹ and chlorosilylenes [$:\text{SiCl}_2$ and $:\text{Si}(\text{H})\text{Cl}$]¹⁷⁰⁻¹⁷² have also been observed as reaction intermediates in the chemical vapor deposition of silicon from silane (SiH_4) and chlorosilanes, respectively.¹⁷³ Despite these successes, stabilization of silylenes at ambient conditions has been a consistent challenge for synthetic chemists.

Lewis bases, specifically N-heterocyclic carbenes, have recently been utilized to stabilize these transient silylenes.¹⁷⁴⁻¹⁷⁵ Indeed, Roesky *et al.* have reported a Lewis-base-complexed chlorosilylene,⁵⁵ and Robinson *et al.* synthesized a carbene-stabilized dichlorobis-silylene by the potassium graphite reduction of $\text{L}:\text{SiCl}_4$ ($\text{L} = \text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}\}_2$).³⁶ The parent chlorosilylene, $:\text{SiCl}_2$, has been synthesized by both N-heterocyclic carbene-mediated reductive elimination of HCl from HSiCl_3 and potassium graphite reduction of $\text{L}:\text{SiCl}_4$ ($\text{L} = \text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}\}_2$).⁷¹ Interestingly, $\text{L}:\text{SiCl}_2$ complexes have shown reactivity towards organic and organometallic species.¹⁷⁴ In addition to these silylene species, the parent silylene ($:\text{SiH}_2$) has been stabilized by donor (carbene)-acceptor (group 13 Lewis acids) coordination.^{43, 176} There have been recent unsuccessful attempts to synthesize the parent monochlorosilylene [$:\text{Si}(\text{H})\text{Cl}$] via N-heterocyclic carbene-mediated HCl elimination from SiH_2Cl_2 ,¹⁷⁷ highlighting the difficulty when synthesizing these unstable silylene species.

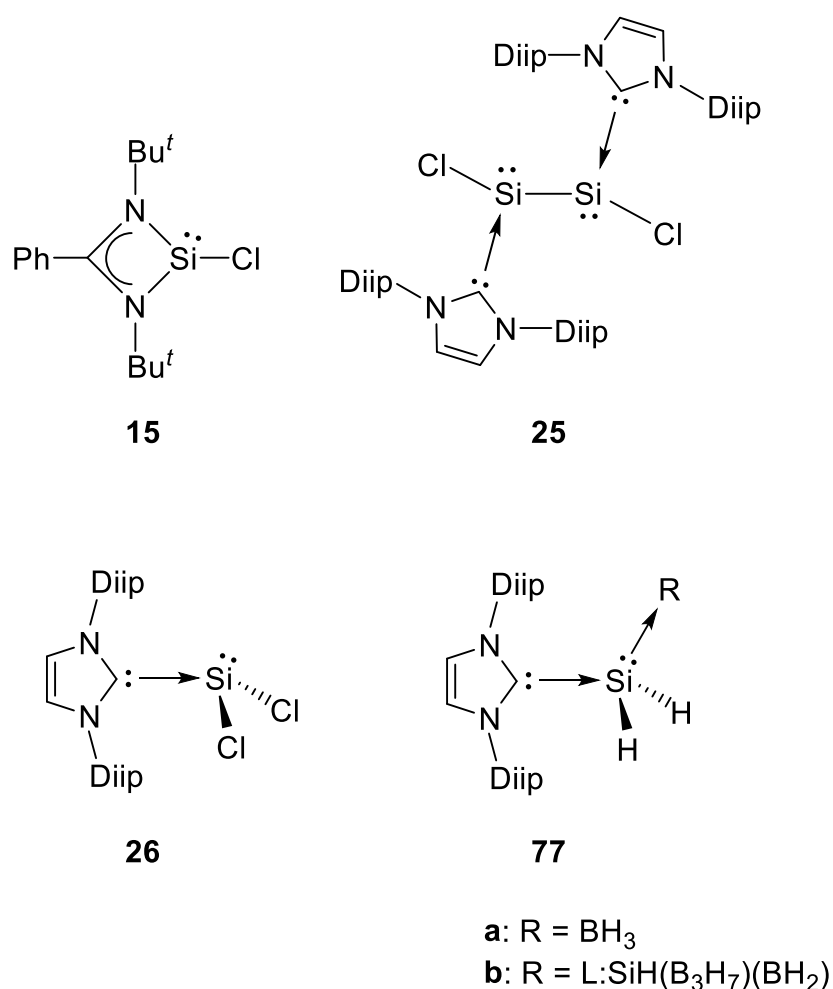
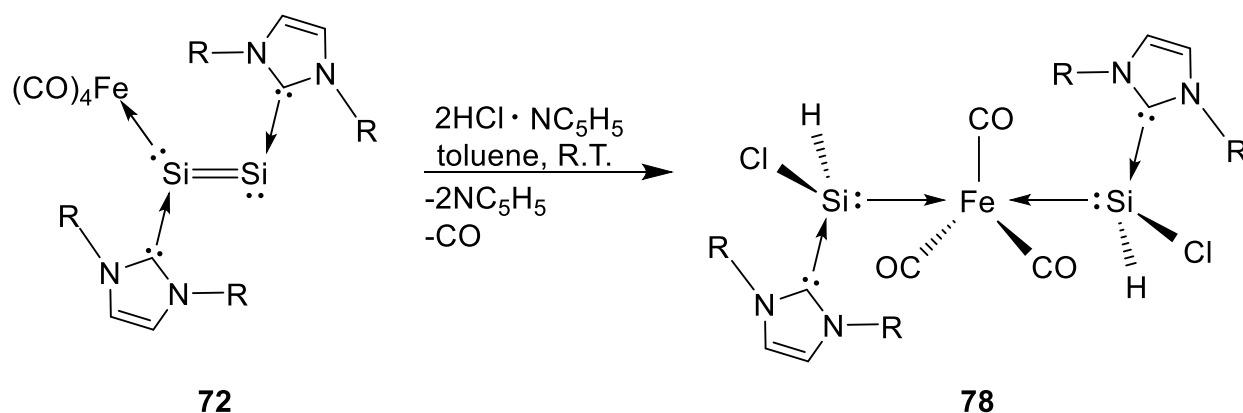


Figure 16. Lewis base-stabilized chlorosilylenes, and “push-pull” stabilized parent silylene (Diip = 2,6-diisopropylphenyl).

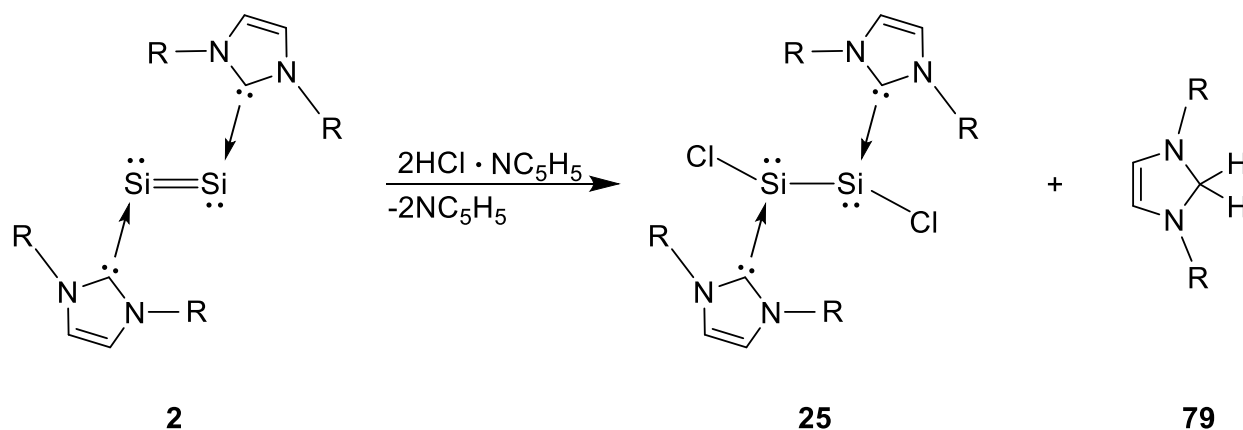
Exploring the transition metal chemistry of carbene-stabilized disilicon(0), L:Si=Si:L (L: = C{N(2,6-Prⁱ₂C₆H₃)CH₂}₂), both L:Si=Si(CuCl):L (**78**)¹⁴⁰ and L:Si=Si[Fe(CO)₄]:L (**72**)¹⁷⁸ have been synthesized by this laboratory. Herein, we report the synthesis, structure, and computations of a “push-pull”-stabilized parent monochlorosilylene [:Si(H)Cl] (**78**) via reaction of **72** with pyridine hydrochloride (HCl·NC₅H₅) (Scheme 47). Compound **78** represents the first example of the parent monochlorosilylene stabilized at ambient conditions.⁴⁴

The reaction of carbene-stabilized disilicon(0) with electrophilic Brookhart’s acid ([H(Et₂O)₂][B(Ar^F)₄, Ar^F = C₆H₃-3,5-(CF₃)₂)¹⁷⁹ gives a carbene-complexed HSi₂⁺ cation.¹⁸⁰

Additionally, pyridine hydrochloride has been used by this laboratory to prepare the HP_2^+ cation by reaction with carbene-stabilized diphosphorus (L:P-P:L , $\text{L:} = \text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}\}_2$).¹⁸¹ Low-temperature reaction of **72** with two equivalents of pyridine hydrochloride (1:2 ratio) in toluene gives the neutral compound **78** (orange, 58.0% yield). Reaction of **72** with pyridine hydrochloride in a 1:1 ratio only affords a mixture of **72** and **78**. It is of note that bis(carbene-silylene) transition metal compounds with a $[\text{L:}\rightarrow\text{silylene:}]_2\rightarrow\text{transition metal}$ bonding structure have been hypothesized as intermediates in the synthesis of disilene transition metal complexes.¹⁸² The analogous reaction of carbene stabilized disilicon(0) (**2**) with pyridine hydrochloride was also investigated, in order to ascertain the importance of the iron carbonyl unit in **72**. The 1:2 reaction ($\text{2:HCl}\cdot\text{NC}_5\text{H}_5$) gives a complicated mixture of products, where carbene-stabilized dichlorobis-silylene (**25**) and protonated free N-heterocyclic carbene (**79**), as well as free carbene (:L) and its precursor ($\text{L:H}^+\text{Cl}^-$) were identified by ^1H NMR spectroscopy (Scheme 48).^{36, 183} Indeed, the iron carbonyl-modified core in **72** exhibits unique reactivity towards pyridine hydrochloride compared to the Si_2 core in **2**, highlighting the importance of the $\text{Fe}(\text{CO})_4$ -modification of carbene-stabilized disilicon(0). Although the mechanism for the formation of **78** is still unknown, we hypothesize that L:Si(H)Cl ($\text{L:} = \text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}\}_2$) may participate as an unstable intermediate, which then decomposes to give a mixture of **25**, **79**, and other byproducts.



Scheme 47. Synthesis of the parent monochlorosilylene (**78**).



Scheme 48. Reaction of carbene-stabilized-disilicon(0) (**2**) with $\text{HCl} \cdot \text{NC}_5\text{H}_5$.

Analysis of the single crystal X-ray structure of **78** reveals two four-coordinate Si(II) atoms, where each Si(II) accepts one lone pair of electrons from the carbene ligand and donates an electron pair to the central $\text{Fe}(\text{CO})_3$ unit. The Si–C (1.958 Å, av.), Si–Cl (2.128 Å, av.), and Si–Fe (2.213 Å, av.) bond distances are comparable to those [$d_{\text{Si-C}} = 1.958(3)$ Å; $d_{\text{Si-Cl}} = 2.0890(12)$ and $2.0965(14)$ Å; $d_{\text{Si-Fe}} = 2.229(11)$ Å] for $\text{L}:\text{SiCl}_2[\text{Fe}(\text{CO})_4]$ ($\text{L} = \text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}\}_2$).¹⁴⁴ The Si–Fe bond in **72** [2.3265(10) Å] is longer than that in **78** (2.213 Å, av.). The central iron atom in **78** exists in a distorted trigonal bipyramidal geometry, with three CO ligands at the equatorial positions and the two $:\text{Si}(\text{H})\text{Cl}$ units at the axial positions.

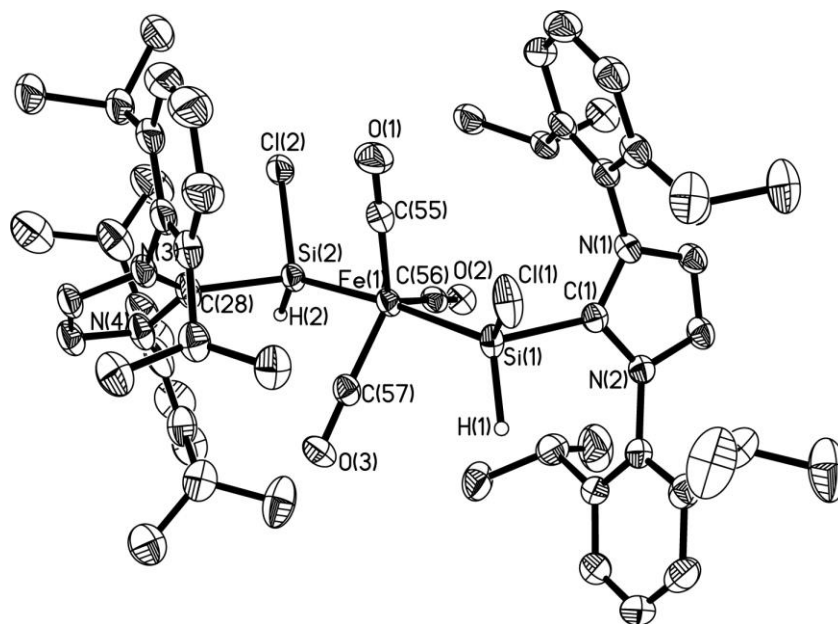


Figure 17. Molecular structure of **78**. Thermal ellipsoids represent 30% probability. Hydrogen atoms attached to carbons have been omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)–C(1), 1.955(5); Si(1)–Cl(1), 2.135(5); Si(1)–Fe(1), 2.213(3); Si(2)–C(28), 1.957(5); Si(2)–Cl(2), 2.127(3); Si(2)–Fe(1), 2.189(3); C(1)–Si(1)–Cl(1), 98.7(2); Cl(1)–Si(1)–Fe(1), 117.03(19); C(1)–Si(1)–Fe(1), 120.42(18); Si(1)–Fe(1)–Si(2), 172.77(18); Si(1)–Fe(1)–C(55), 91.7(2); C(28)–Si(2)–Cl(2), 95.14(18); Cl(2)–Si(2)–Fe(1), 117.97(15); C(28)–Si(2)–Fe(1), 122.49(19).

The two SiCl_2 units in $[\text{Co}(\text{CO})_3(\text{SiCl}_2\text{L})_2]^+[\text{CoCl}_3(\text{THF})]^-$ ($\text{L} = \text{C}\{\text{N}(2,6\text{-Pr}_2\text{C}_6\text{H}_3)\text{CH}\}_2$) only exhibit one singlet in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (44.11 ppm), while compound **78**, with two chiral silicon centers, exhibits two adjacent $^{29}\text{Si}\{^1\text{H}\}$ NMR resonances at 44.02 and 45.32 ppm, due to the presence of two diastereoisomers.¹⁸⁴ Two silicon hydride ^1H NMR resonances (6.20 and 6.22 ppm in C_6D_6) are also observed for **78**, and indicate an approximately 1:2 population of the two diastereoisomers. The ^1H -coupled ^{29}Si NMR spectrum of **78** shows a coupling constant, $^1J_{\text{Si-H}} = 195$ Hz (av.), which matches well with the coupling constant [$^1J_{\text{Si-H}} = 192$ Hz (av.)] of low-intensity ^{29}Si satellites observed in the ^1H NMR spectrum. The Si–H stretching band ($\nu = 2103$

cm⁻¹) in the IR spectrum of **78** aligns with the Si–H stretching band ($\nu = 2118\text{ cm}^{-1}$) of L₂SiH₂Cl₂ (L: = C{N(2,6-Prⁱ₂C₆H₃)CH}₂).¹⁷⁷ It is also of note that the three CO ligands in [Co(CO)₃(SiCl₂L)₂]⁺[CoCl₃(THF)]⁻ (L: = C{N(2,6-Prⁱ₂C₆H₃)CH}₂) are characterized as a singlet ¹³C NMR resonance (199.3 ppm), and as three distinct IR bands (1969, 1994, 2052 cm⁻¹), while the three CO groups in **78** exhibit two adjacent ¹³C NMR resonances (216.2 and 216.5 ppm) and five IR stretching bands [1823, 1832, 1856 (br), 1934, and 1941 cm⁻¹], providing further evidence of the existence of two diastereoisomers of **78**. Density functional theory computations at the B3LYP/6-311+G** level were performed on the simplified model, **78-H** [optimized in C₂ symmetry, L: = :C(NHCH)₂] (Figure 19). The computed bond distances for **78-H** [Si–C (1.963 Å), Si–Cl (2.178 Å), and Si–Fe (2.227 Å)] match well with the experimental values [Si–C (1.958 Å, av.), Si–Cl (2.128 Å, av.), and Si–Fe (2.213 Å, av.)] obtained for **78**. The Wiberg bond index of the Si–Fe bond (0.43) in **78-H** is comparable to that for the Si–Fe bond in **72-Me** (0.69) [L: = :C(N(Me))(CH)₂].¹⁷⁸ The positive natural charge (+0.89) on each silicon atom and the negative charge (-0.74) on the central iron atom indicate the dative character of the Si–Fe bonds in **78-H**.

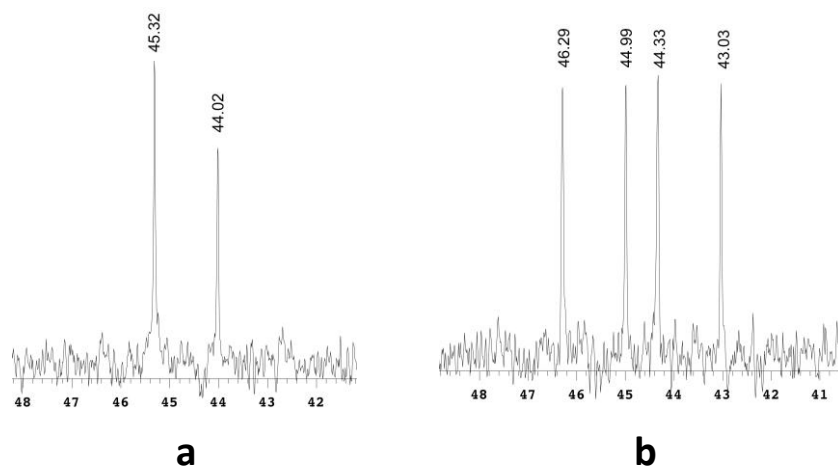


Figure 18. a) ²⁹Si{¹H} NMR resonances of **78**. b) ¹H-coupled ²⁹Si NMR spectrum of **78**.

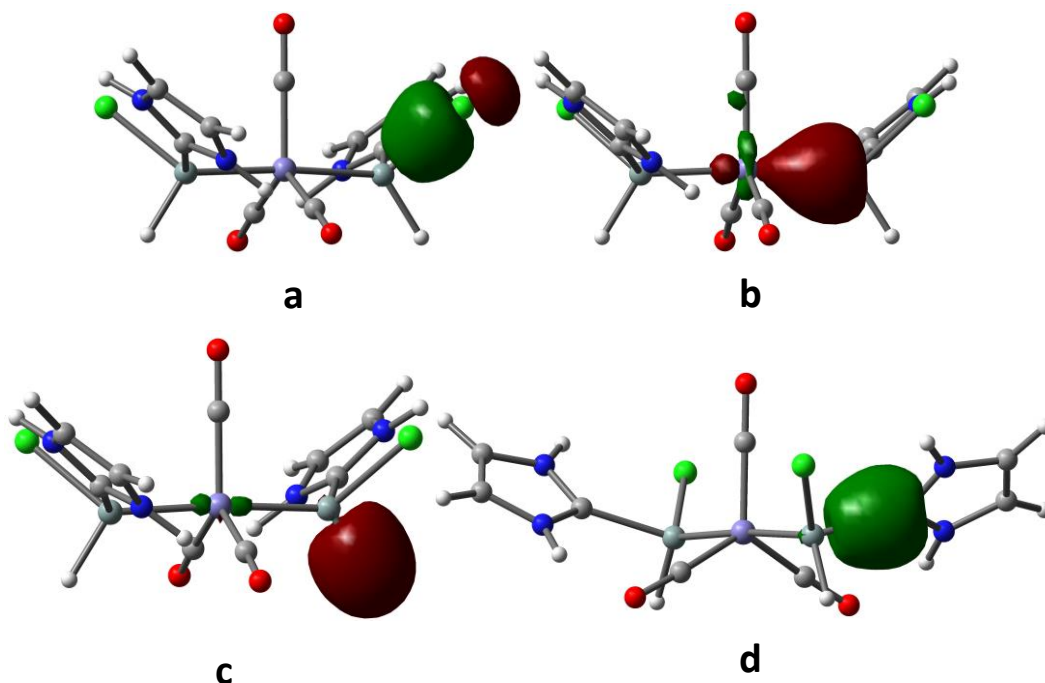


Figure 19. Selected localized molecular orbitals (LMOs) of **78-H**: (a) Si–Cl σ -bonding orbital; (b) Si–Fe σ -bonding orbital; (c) Si–H σ -bonding orbital; (d) Si–C_{NHC} σ -bonding orbital.

The unique platform of the iron-carbonyl-modified disilicon carbene complex, **72**, allows access to a donor-acceptor-stabilized parent monochlorosilylene [:Si(H)Cl], **78**, which exists as two diastereoisomers. Reaction of carbene-stabilized disilicon(0) with $\text{HCl}\cdot\text{NC}_5\text{H}_5$ did not give the carbene-stabilized :Si(H)Cl product, but a mixture of side products, highlighting the importance of the Fe(CO)_4 -modification of carbene-stabilized disilicon(0) in synthesizing the parent monochlorosilylene.

2.3 Facile Conversion of Bis-Silylene to Cyclic Silylene Isomers:

Unexpected C–N and C–H Bond Cleavage

Silylenes (:SiR_2) are highly reactive divalent silicon intermediates.¹⁵⁴⁻¹⁵⁶ Specifically, the parent chlorosilylene (:SiCl_2)¹⁷⁰⁻¹⁷² and the parent silylene (:SiH_2)¹⁶⁹ have been observed as

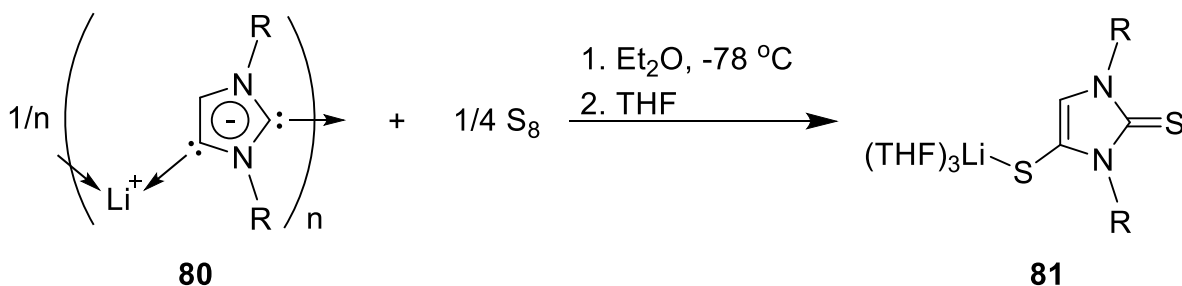
reactive intermediates in the chemical vapor deposition of silicon from silane and chlorosilanes, respectively. The synthesis of the siliconocene and diamidosilylene prompted the investigation into a large number of stable silylenes that have been utilized in organic syntheses, transition metal coordination, catalysis, and small-molecule activation.^{52, 107, 122, 132, 157-159, 185-186}

N-heterocyclic silylenes have been the most widely researched class of cyclic silylenes,^{2, 55, 57} while the cyclic alkyl silylenes⁶⁵ are less prevalent, due to a lack of stabilizing π -donor substituents. In contrast, acyclic silylenes are generally stabilized by coordination of a Lewis base.⁶⁸ Only recently have stable, acyclic, two-coordinate silylenes been reported.^{73-76, 187} It is notable that the boryl(amino)silylene and the diaminosilylene have participated in H₂, O₂, and NH₃ activation.^{74, 76}

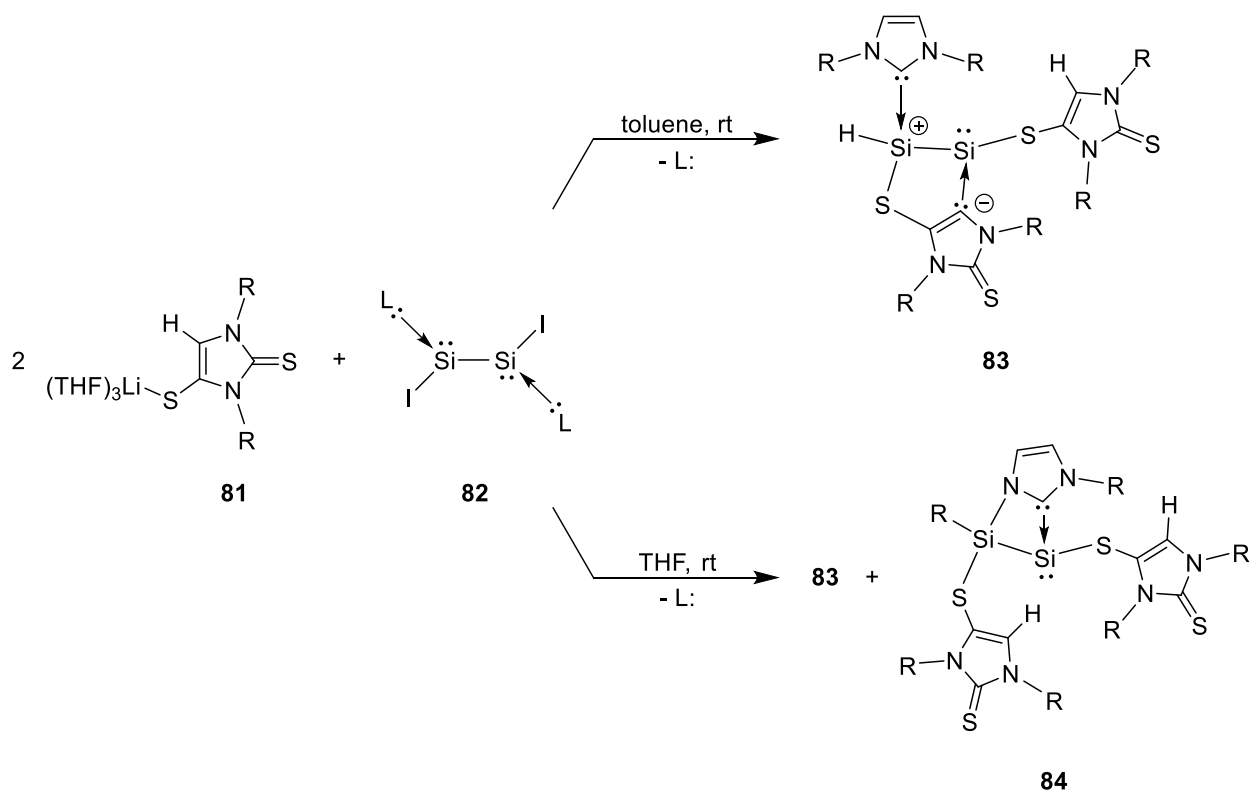
The Robinson group prepared an N-heterocyclic carbene-stabilized bis-silylene [L:(Cl)Si-Si(Cl):L] via KC₈ reduction of L:SiCl₄ [L: = C{N(2,6-Prⁱ₂C₆H₃)CH}₂].³⁶ Subsequently, the synthesis of [L:(X)Si-Si(X):L] (X = Cl, Br, I) by combination of carbene-stabilized disilicon(0) (L:Si=Si:L) (L: = C{N(2,6-Prⁱ₂C₆H₃)CH}₂) with 1,2-dihaloethanes was reported.⁷⁰ Reaction of dihalo(bis-silylenes) with anionic ligands may provide new avenues to access novel unusual low-oxidation-state organosilicon species. Herein, we report thiolate (**81**)-mediated conversion of bis-silylene (**82**) to five- and four-membered cyclic silylene isomers via unexpected C–H and C–N bond cleavage, respectively. Indeed, compounds **83** and **84** are the first cyclic silylenes containing a silicon-silicon bond. While silylenes are known to participate in C–H bond activation of organic substrates,^{59, 188-193} compound **83** is the first “SiI₂” insertion into an olefinic C–H bond. Main group species have recently received recognition in the C–N bond activation of NHCs.¹⁹⁴⁻¹⁹⁵ Additionally, alkali metal-mediated C–N bond cleavage of saturated NHCs¹⁹⁶⁻¹⁹⁷ and N-heterocyclic guanidine¹⁹⁸ has been reported. Main group (*i.e.*, beryllium, silicon, boron, and

aluminum) hydrides and Lewis acids are also known to prompt imidazole ring expansion reactions through C_{NHC}–N bond cleavage.¹⁹⁹⁻²⁰⁷ Reactive borylene intermediates have been reported to insert into a C_{phenyl}–N bond of N-heterocyclic olefins.²⁰⁸ Compound **84** is the first example of silicon(I)-mediated cleavage of a C–N bond in NHCs.

The Robinson group recently synthesized an imidazole-based thiolate (**81**) by disulfurization of anionic N-heterocyclic dicarbene (**80**) (Scheme 49). Subsequent reaction of **81** with carbene-stabilized bis-silylene **82** in a 2:1 ratio in toluene gave compound **83** in 52.5% yield, while the same reaction in THF gave the cyclic silylene isomers **83** and **84** in an approximately 7:1 ratio (based on ¹H NMR data) (Scheme 50). Compounds **83** and **84** may be isolated as yellow and colorless crystals, respectively. Interestingly, there does not appear to be an interconversion between **83** and **84**.



Scheme 49. Synthesis of imidazole-based thiolate (**81**).



Scheme 50. Thiolate (**81**)-mediated conversion of bis-silylene (**82**) to cyclic silylene isomers (**83** and **84**).

Compound **83** contains a five-membered silylene heterocycle, which is formed through the “ Si_2^1 ” insertion into the imidazole C–H bond of the complexed thiolate **81** (Figure 20). The $\text{C}_2\text{Si}_2\text{S}$ ring (Si-S-C-C torsion angle = -30.2°) is obviously bent, which is likely due to the steric repulsion of the bulky substituents. This large steric repulsion also leads to slow rotation of the NHC ring about the $\text{C}_{\text{NHC}}\text{-Si}$ bond, as two ^1H NMR resonances are observed for the NHC ring protons.²⁰⁹ The Si–Si bond in **83** [2.349(2) Å] is slightly shorter than those in $\text{L}:(\text{X})\text{Si-Si}(\text{X})\text{L}$, ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)^{36, 70} and the computed structure, **83-Ph** (2.428 Å), but is close to that for the sum of the silicon covalent radii (2.34 Å).¹⁴⁹ Natural bond order (NBO) analysis of **83-Ph** reveals that the Si–Si σ -bond is polarized primarily (64.4%) towards Si(1) (32.7% s-, 67.1% p-, 0.2% d-character) and only 35.6% towards Si(2) (8.6% s-, 90.7% p-, 0.7% d-character) (Figure 22). The Si(1) atom has

a positive charge of +0.63, and the C(30) atom has a charge of -0.34. The H(1) atom on the four-coordinate Si(1) in **83** has a ^1H NMR resonance of 4.61 ppm and was found crystallographically in the difference Fourier map. The Si–H coupling constants ($^1J_{\text{Si-H}} = 195$ Hz and $^2J_{\text{Si-H}} = 20$ Hz) in the proton-coupled ^{29}Si NMR spectrum of **83** match with those found for low intensity ^{29}Si satellites in the ^1H NMR spectrum of **83** ($^1J_{\text{Si-H}} = 196$ Hz and $^2J_{\text{Si-H}} = 20$ Hz), as well as the average $^1J_{\text{Si-H}}$ value (195 Hz) observed in the proton-coupled ^{29}Si NMR spectrum of a “push-pull”-stabilized parent monochlorosilylene [$:\text{Si}(\text{H})\text{Cl}$] (**78**) (Figure 21).⁴⁴ Additionally, the Si–H IR stretching band ($\nu = 2109\text{ cm}^{-1}$) for **83** is close to that for both **78** ($\nu = 2103\text{ cm}^{-1}$) and for $\text{L}_2\text{SiH}_2\text{Cl}_2$ ($\nu = 2118\text{ cm}^{-1}$) [$\text{L}: = \text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}\}_2$].¹⁷⁷ The distorted trigonal pyramidal geometry around the Si(2) atom is consistent with the geometry of the silicon atom in other three-coordinate silylenes, and supports the existence of a silicon-based electron lone pair. The C(30)–Si(2) [1.941(6)] Å and C(1)–Si(1) [1.909(6)] Å bond distances in **78** compare well to the $\text{C}_{\text{NHC}}\text{–Si}$ bond distances [1.929(7)–1.943(2)] Å in [$\text{L}:(\text{X})\text{Si}(\text{X})\text{Si}(\text{X})\text{L}$], X = Cl, Br, and I].^{36, 70} Additionally, the Si–Si bonds in **83** [2.183(2) and 2.263(2)] Å are slightly longer than those reported for $\text{Si}(\text{SAr}_2)$ [$\text{Ar} = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_2\text{-2,4,6-Me}_3)_2$] [2.1560(5) and 2.1607(5)] Å.⁷³

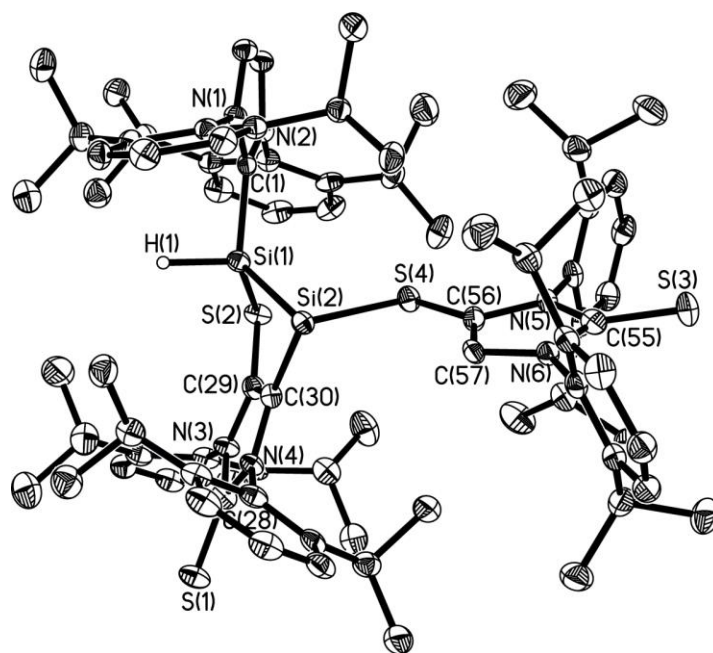


Figure 20. Molecular structure of **83**. Thermal ellipsoids represent 30% probability. Hydrogen atoms attached to the carbons have been omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)–H(1), 1.441(19); Si(1)–Si(2), 2.349(2); Si(1)–C(1), 1.909(6); Si(1)–S(2), 2.183(2); Si(2)–S(4), 2.263(2); Si(2)–C(30), 1.941(6); C(1)–Si(1)–Si(2), 123.89(18); S(2)–Si(1)–Si(2), 106.57(9); Si(1)–Si(2)–S(4), 93.40(8); Si(1)–Si(2)–C(30), 77.33(17).

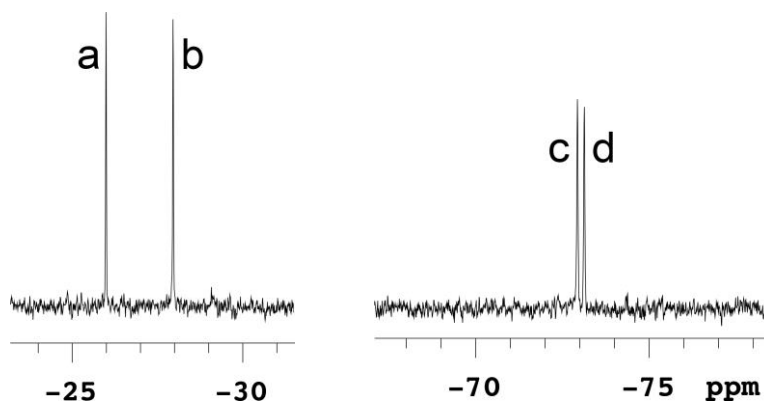


Figure 21. Proton-coupled ^{29}Si NMR spectrum of **83** [δ (ppm): for Si(1), a = -26.00, b = -27.96; for Si(2), c = -72.93, d = -73.13].

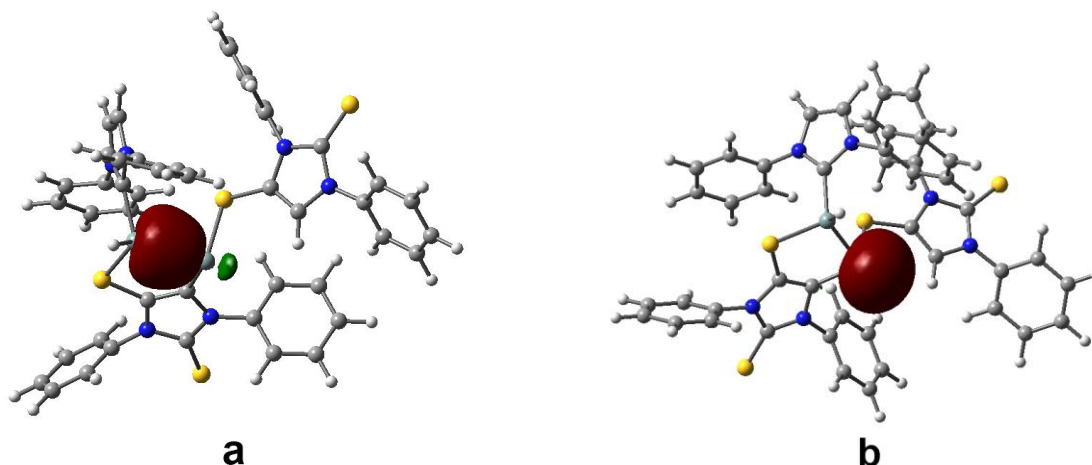


Figure 22. Selected natural bond orbitals (NBOs) of **83-Ph**. (a) Si–Si σ bonding orbital; (b) silicon-based lone pair orbital.

The X-ray structure of **84** suggests that a silylene center inserts into the C(16)–N(1) bond of the carbene ligand to give the nonplanar four-membered CNSi₂ silylene ring, with a thiolate ligand present both above and below the ring (Figure 23). Compared to the single imidazole ¹H NMR resonance present in the ¹H NMR for **83** (6.30 ppm), **84** exhibits two imidazole ¹H NMR resonances (5.20 and 6.16 ppm). The distorted trigonal pyramidal geometry found at the Si(2) atom in **83** is also found in the Si(1) atom in **84**, suggesting the presence of a Si(1)-based electron lone pair. The Si–Si bond in **84** is polarized towards the four-coordinate Si(2) atom [62.9% toward Si(2) and 37.1% toward Si(1) for model compound (**84-Ph**)] (Figure 24). The Si–Si bond distance [2.4164(11) Å] in **84** is only 0.07 Å longer than the Si–Si bond distance [2.349(2) Å] in **83**, corresponding to the WBI values for the Si–Si bonds (0.82 for **84-Ph** and 0.85 for **83-Ph**), and also compares well to the computed Si–Si bond distance (2.463 Å) in **84-Ph**. The two ²⁹Si NMR resonances (+2.21 and -56.73 ppm) found for **84** correspond to the four- and three-coordinate silicon atoms [*i.e.*, Si(2) and Si(1)], respectively, and are shifted downfield compared to those in **83** [-27.00 ppm for Si(1) and -72.98 ppm for Si(2)]. The C_{NHC}–Si [1.952(3) Å] and S–Si

[2.1502(11) and 2.2181(11) Å] bond distances in **84** match well to those in **83** ($d_{\text{C}(1)-\text{Si}(1)} = 1.909(6)$ Å, $d_{\text{S}-\text{Si}} = 2.183(2)$ and $2.263(2)$ Å], and the Si–N bond distance [1.838(3) Å] is comparable to reported Si–N_{imidazole} bond distances [1.759(1)–1.837(3) Å].^{210–211}

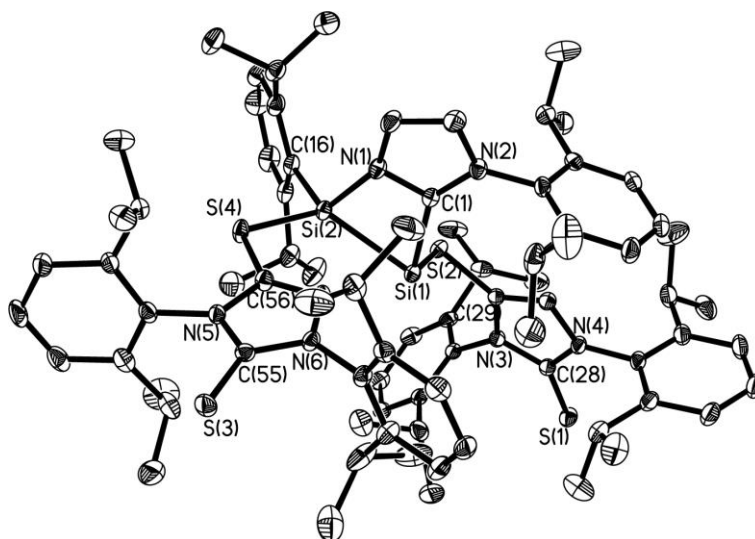


Figure 23. Molecular structure of **84**. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)–Si(2), 2.4164(11); Si(1)–C(1), 1.952(3); Si(1)–S(2), 2.2181(11); Si(2)–N(1), 1.838(3); Si(2)–C(16), 1.889(3); C(1)–Si(1)–Si(2), 67.84(9); C(1)–Si(1)–S(2), 100.20(9); N(1)–Si(2)–Si(1), 78.78(9); Si(1)–Si(2)–S(4), 125.49(5); Si(1)–Si(2)–C(16), 126.58(10).

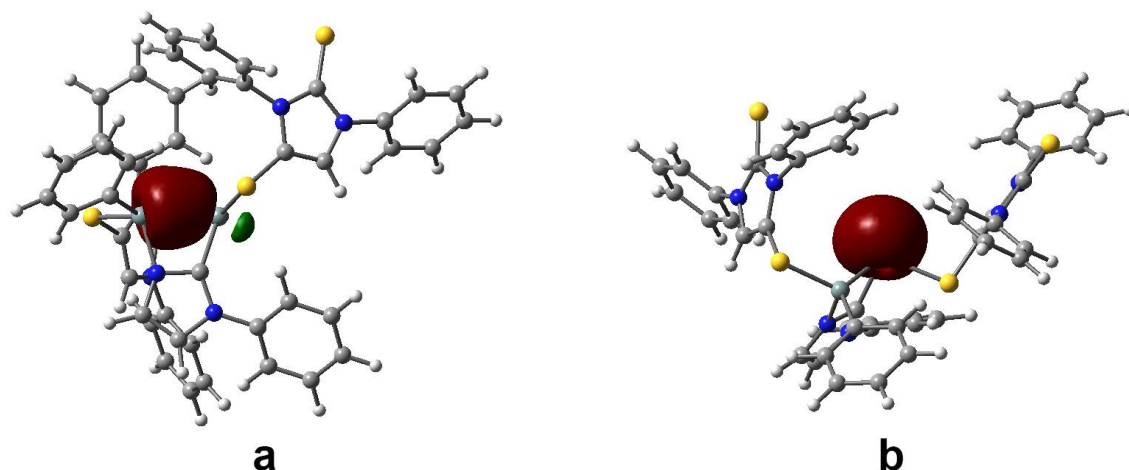


Figure 24. Selected natural bond orbitals (NBOs) of **84-Ph**. (a) Si–Si σ bonding orbital; (b) silicon-based lone pair orbital.

The mechanism of the synthesis of **83** and **84** is unknown, but it is plausible that **85a** and **85b** are possible intermediates via double thiolate ligand coordination and release of one carbene ligand in **82** (Figure 25). **85a** and **85b** were probed by DFT computations on simplified models (**85a-Me** and **85b-Me**) at the B3LYP/6-311G** level. These computations show that **85a-Me** and **85b-Me** are almost identical in energy (ca. 0.5 kcal/mol difference), so only the bonding of **85a-Me** will be discussed. The Si–Si bond distance in **85a-Me** (2.309 Å) is equidistant between the Si=Si double bond distance [2.2294(11) Å] in L:Si=Si:L [L: = C{N(2,6-Prⁱ₂C₆H₃)CH}₂] (0.08 Å shorter than in **85a-Me**) and the Si–Si single bond distance in **82** [2.3909(9) Å] (0.08 Å longer than in **85a-Me**). The relatively short Si–Si single bond distance in **85a-Me**, and the WBI value of 1.33 for the Si–Si single bond suggest that the Si–Si bond in **85a-Me** possesses some amount of double bond character. NBO analysis of **85a-Me** shows that both the Si–Si σ -bonding orbital (67.8%) and π -bonding orbital (69.9%) are polarized towards the three-coordinate Si(1) atom (Figure 26). The Si–Si π -bonding orbital has majorly p-character [99.2% p of Si(1) and 94.7% p of Si(2)], while the Si–Si σ -bonding orbital involves the overlap of the approximately sp

hybridized S(1) atomic orbital (47.2% s, 52.5% p, 0.3% d) with the Si(2) atomic orbital having mostly p-character (8.8 % s, 90.3 % p, 0.9 % d). The two-coordinate Si(2)-based lone pair orbital contains primarily s-character (77.5% s, 22.5 % p, 0.0 % d). Since two-coordinate acyclic silylenes have previously been employed in H₂, O₂, and NH₃ activation,⁷⁵⁻⁷⁶ the two reactive sites present in both **85a** and **85b** (*i.e.*, asymmetric and polarized Si=Si double bond, and the two-coordinate silylene center) could facilitate the unexpected C–H and C–N bond cleavage involved in the formation of **83** and **84**, respectively.

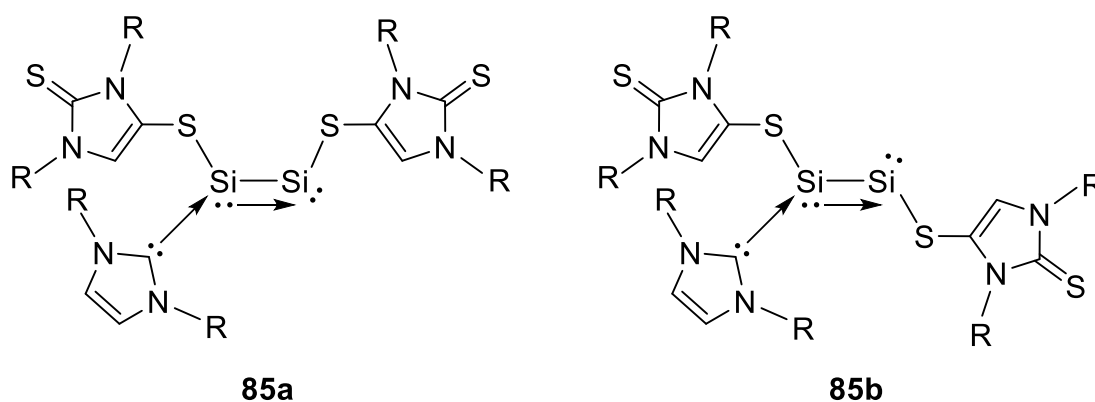


Figure 25. Proposed intermediates **85a** and **85b**, containing a Si^I₂ unit with an asymmetric Si=Si double bond.

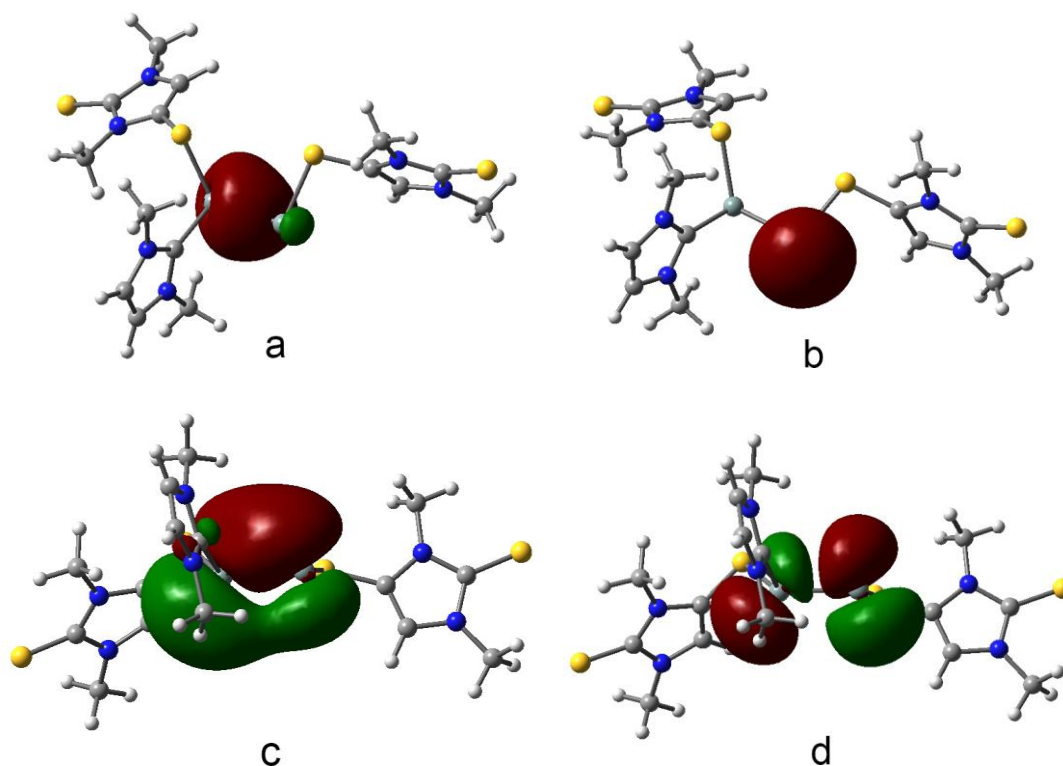


Figure 26. Natural bond orbitals of **85a-Me**. (a) Si–Si σ bonding orbital; (b) silicon-based lone pair orbital; (c) Si–Si π bonding orbital; (d) Si–Si π^* antibonding orbital.

2.4 1,3,2-Diazaborole-Derived Carbene Complexes of Boron

Prior to the groundbreaking synthesis of Bertrand's (phosphine)(silyl)carbene^{93, 212} and Arduengo's synthesis of the first N-heterocyclic carbene,⁵ carbenes were considered far too reactive to isolate.⁹⁴ Nowadays, NHCs are ubiquitous, and are utilized organic and transition metal catalysis,²¹³ as well as in low-oxidation state main group chemistry.^{9, 95, 174, 214-219} Following the synthesis of 'normal' NHCs (**I**), 'abnormal' NHCs (*a*NHCs) (**II**) were synthesized, and have seen applications in catalysis, due to *a*NHCs having stronger electron-donating properties than normal NHCs (Figure 27).²²⁰⁻²²⁵ Additionally, the first metal-free *a*NHC was recently reported.²²⁶ This group reported the lithiation of an NHC to give an anionic N-heterocyclic dicarbene (NHDC) (**III**),

which contains both C2 and C4 carbene centers (Figure 27).²²⁷⁻²²⁸ Subsequently, multi-anionic NHDCs were also reported.²²⁹⁻²³⁰ Indeed, NHDCs are becoming more popular in main group and transition metal chemistry.²³¹

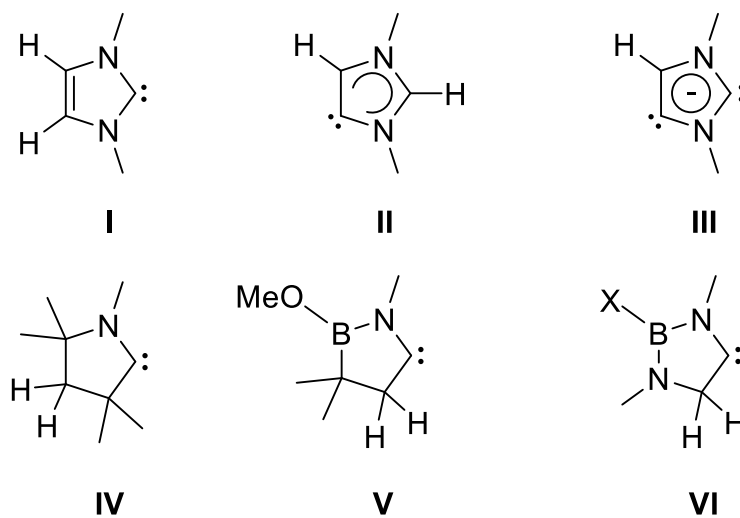


Figure 27. Imidazole-based carbenes (**I-III**), CAAC (**IV**), 1,2-azaborole-derived CAAC (**V**), and 1,3,2-diazaborole-derived carbene (**VI**).

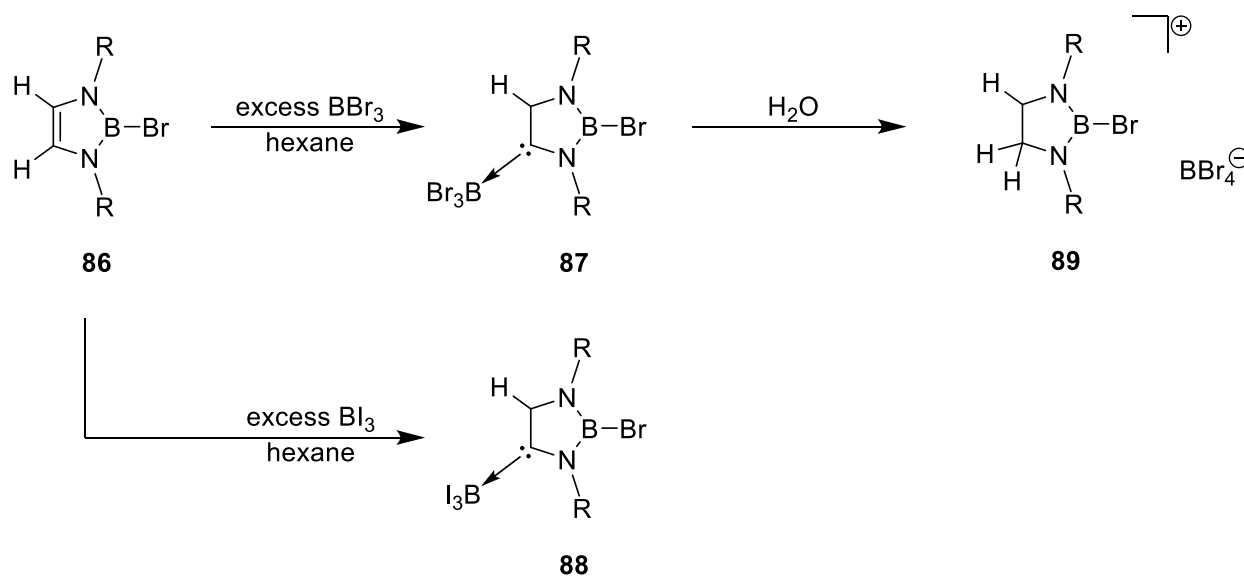
In addition to NHDCs, usage of the cyclic (alkyl)(amino)carbenes (CAACs) (**IV**),¹⁰ developed by Bertrand, has increased (Figure 27).⁹⁵⁻⁹⁷ CAACs are both stronger σ -donors and π -acceptors than NHCs, due to their higher energy HOMO and the lower energy LUMO when compared to NHCs. Additionally, the singlet-triplet gap for CAACs is considerably smaller than for NHCs,^{95, 232} which is consistent with our own computations at the B3LYP/6-311G** level (Figure 29).

Kinjo *et al.* recently reported the synthesis of 1,2-azaborole-derived CAAC (**V**)-borane adducts *via* a borane-initiated 1,2-hydrogen migration.¹² This discovery may lead to unique methods by which access to asymmetrical diborenes and allenic diborenes could be obtained.^{12, 233} Prior to Kinjo's breakthrough, only transient carbene formation from alkenes *via* a 1,2-hydrogen migration had been reported.²³⁴⁻²³⁸ While 2-bromo-1,3,2-diazaborole has allowed access to

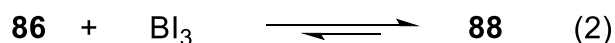
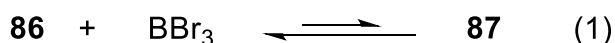
nucleophilic 1,3,2-diazabororyllithium and its main group and transition metal derivatives, the direct utility of 2-bromo-1,3,2-diazaborole has not been investigated. We report the synthesis, structures, and computations of 1,3,2-diazaborole-derived carbene-boron halides *via* 1,2-hydrogen migration.

Reaction of 2-bromo-1,3,2-diazaborole (**86**) with excess BBr₃ in hexane affords 2-bromo-1,3,2-diazaborole-derived carbene-boron bromide complex (**87**) in quantitative yield (based on ¹H NMR data) (Scheme 51). While the 1,2-azaborole-derived CAAC-boron halides do not dissociate in organic solvents, **87** exists in dynamic equilibrium with **86**. This equilibrium is supported by the three sets of ¹¹B NMR resonances for the C₆D₆ solution of **87** [*i.e.*, +30.28 and -14.42 ppm (**87**), +20.10 ppm (**86**), and +37.14 ppm (BBr₃)] (Figure 28). The borole ¹H NMR resonances in C₆D₆ (5.87 ppm for **87** and 6.13 ppm for **86**) indicate an approximate 2:1 molar ratio (**86**:**87**) in the equilibrium mixture (eq. (1), Scheme 52). Thus, the equilibrium lies to the left in the dissociation reaction of **87**. Addition of BBr₃ to the reaction mixture shifts the equilibrium to the right. Moreover, our computations suggest that 1,2-azaborole-derived carbenes, like bicyclic (alkyl)(amino)carbenes (BICAACs),²³⁹ are even stronger σ -donors and π -acceptors than CAACs (considering the relatively higher energy HOMO and lower energy LUMO of **V** than **IV**) (Figure 29). Additionally, the singlet-triplet gap of **V** (35.3 kcal mol⁻¹) is smaller than that for CAAC (**IV**) (49.5 kcal mol⁻¹) (Figure 29). In comparison, 1,3,2-diazaborole-derived carbene (**VI**) has an obviously lower energy HOMO, and thus a weaker electron-donating capability than **V** (Figure 29). This could explain why **87** readily undergoes partial dissociation. Compound **87** may also be hydrolyzed by trace amounts of moisture, giving the protonated byproduct **89** as colorless crystals (Scheme 51). Compound **89** was only characterized by X-ray single crystal diffraction, as reaction of **86** with HCl does not give the protonated analog of **89**, but rather 2-chloro-1,3,2-diazaborole.

Addition of BF_3 or BCl_3 does not produce the corresponding analogs of **87**, but the parallel reaction of **86** with excess BI_3 yields complex **88** in quantitative yield (Scheme 51). The borole ^1H NMR resonances in C_6D_6 solution of **88** (6.58 ppm for **88** and 6.13 ppm for **86**) indicate an approximate 1:17 molar ratio (**86**:**88**) in the equilibrium mixture. Accordingly, the dissociation reaction of **88** lies largely to the right, favoring the formation of **88** (eq. (2), Scheme 52). An explanation for this may be due to the increase of the Lewis acidity of the boron trihalides down the group. The ^{11}B NMR spectrum of **88** in C_6D_6 at room temperature shows resonances for **88** (+30.38 ppm and -69.52 ppm), **86** (+20.21 ppm), and BI_3 (-8.07 ppm), and also two resonances for an uncharacterized species (+25.26 ppm and -45.60 ppm) (Figure 30).



Scheme 51. Synthesis of **87**, **88**, and **89**.



Scheme 52. Dynamic equilibrium of **87** and **88**.

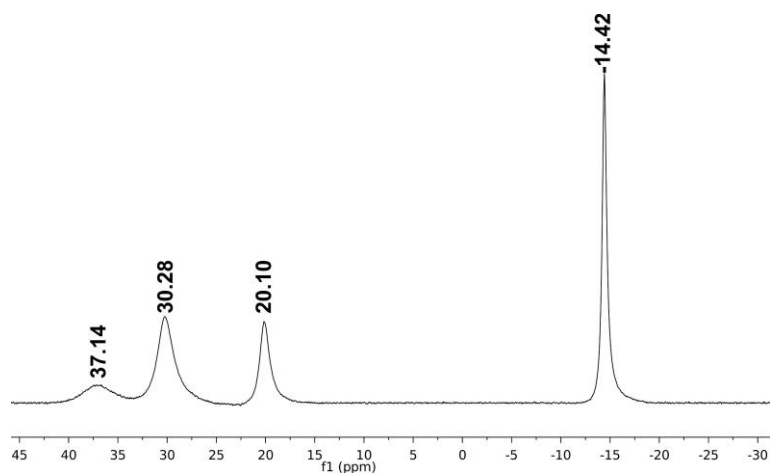


Figure 28. ^{11}B NMR spectrum of **87** in C_6D_6 at room temperature.

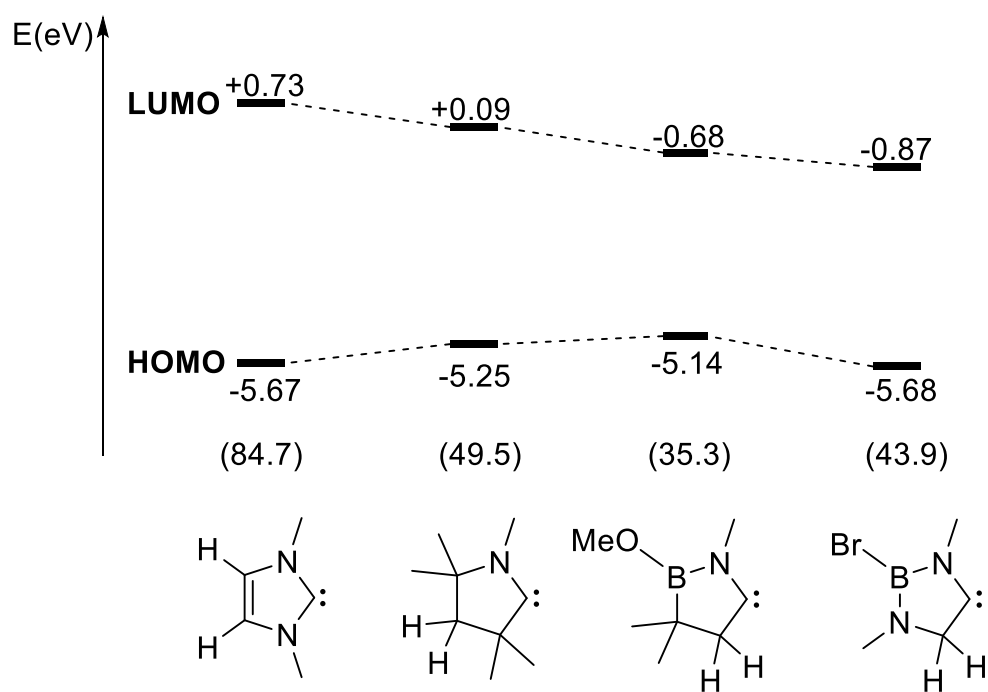


Figure 29. Energy (eV) of the frontier orbitals and ΔE_{ST} (singlet–triplet gap, kcal mol $^{-1}$) of carbenes (**I**, **IV–VI**) calculated at the B3LYP/6-311G** level of theory.

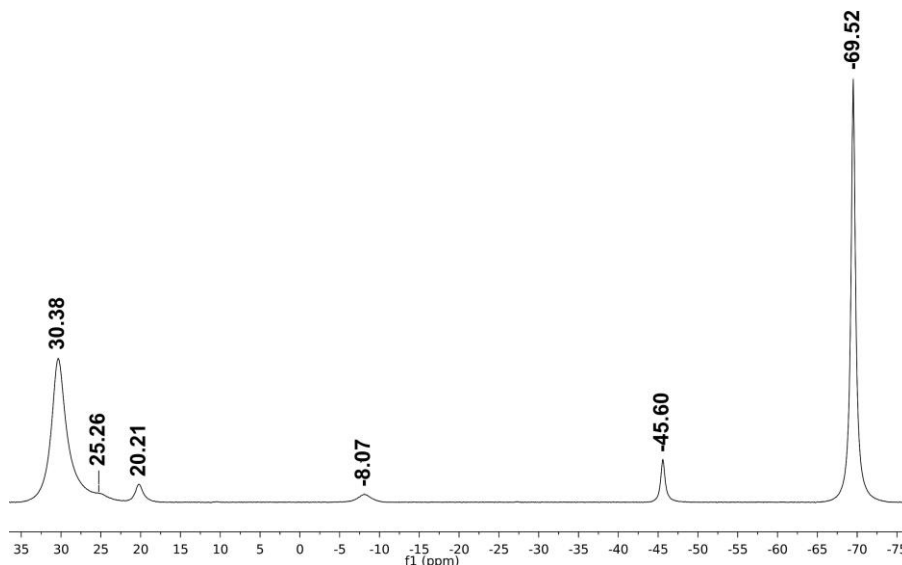


Figure 30. ^{11}B NMR spectrum of **88** in C_6D_6 at room temperature.

Single crystal X-ray structural analysis reveals that compound **87** crystallizes in the orthorhombic space group *Pbca*, and that the asymmetric unit cell contains two independent molecules of **87**. The two hydrogen atoms on the borole-derived carbene ring of **87** were located in the difference Fourier map. The carbon-carbon bond in the carbene ring of **87** [1.488(11) Å, av.] is close to that of the model, **87-Me** (1.498 Å), and is obviously longer than the C=C double bond found in compound **86** [1.330(9) Å], suggesting that **87** contains a C–C single bond [WBI(C–C bond)_{borole ring} of **87-Me** = 1.04] (Figure 31). The C–B single bond in **87** [1.590(12) Å, av.], is comparable to that [1.623(7) Å] of $\text{L}:\text{BBr}_3$ [$\text{L} = \text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}\}_2$],²⁴⁰ and is highly polarized towards the carbene carbon (71.1% toward carbon and 28.9% toward boron for **87-Me** model). The B_{borole}–Br bond distance [1.891(9) Å, av.] in **87** is close to that [1.898(7) Å] for **86** but is longer than those of the BBr_3 moiety in **87** [1.963(10)–2.063(10) Å].

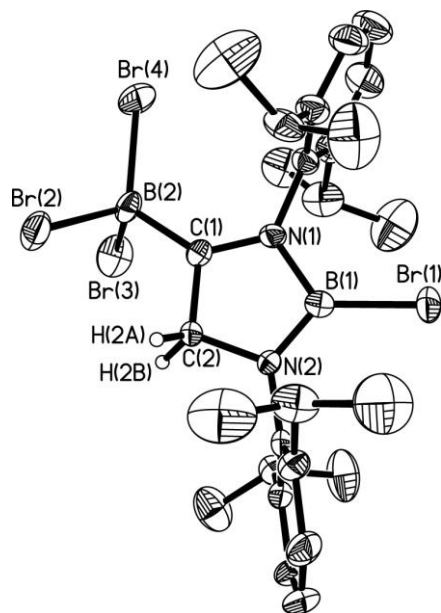


Figure 31. Molecular structure of **87**. Thermal ellipsoids represent 30% probability: hydrogen atoms except for those residing at C(1) and C(2) are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: B(1)–Br(1) 1.888(9), B(2)–C(1) 1.579(11), C(1)–C(2) 1.493(10), B(2)–Br(2) 2.006(10), B(2)–Br(3) 2.063(10), B(2)–Br(4) 1.963(10); N(1)–B(1)–Br(1) 124.1(6), N(1)–C(1)–B(2) 131.7(7), C(2)–C(1)–B(2) 121.1(7).

Compound **88** crystallizes in the orthorhombic space group $P2_12_12_1$ and is isostructural to **87**. Both **87** and **88** exhibit similar C–B, C–C, N–B, C–N and B–Br bond distances. The B–I bond distances [2.200(8)–2.265(8) Å] of **88** are similar to those in the computed model, **88-Me** (Figure 32). Additionally, compound $[\mathbf{89}]^+[\mathbf{BBr}_4]^-$ crystallizes in the monoclinic space group $P2_1/c$. The three hydrogen atoms on the C(1) and C(2) atoms in the heterocycle of $[\mathbf{89}]^+$ were located from the difference Fourier map. The C–C bond in the BN_2C_2 ring of $[\mathbf{89}]^+$ [1.470(5) Å] is only slightly shorter than those in **87** [1.488(11) Å, av] and **88** [1.491(8) Å] (Figure 33).

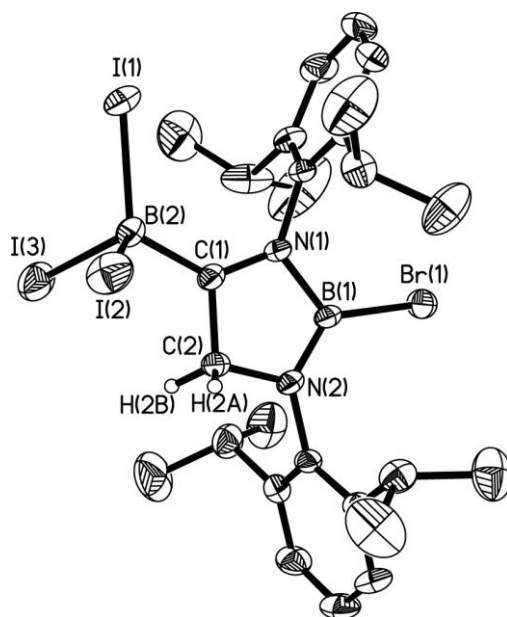


Figure 32. Molecular structure of **88**. Thermal ellipsoids represent 30% probability: hydrogen atoms except for those residing at C(1) and C(2) are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: B(1)–Br(1) 1.899(6), B(2)–C(1) 1.615(9), C(1)–C(2) 1.491(8), B(2)–I(1) 2.200(8), B(2)–I(2) 2.229(8), B(2)–I(3) 2.265(8); N(1)–B(1)–Br(1) 123.6(4), N(1)–C(1)–B(2) 131.7(5), C(2)–C(1)–B(2) 119.9(5).

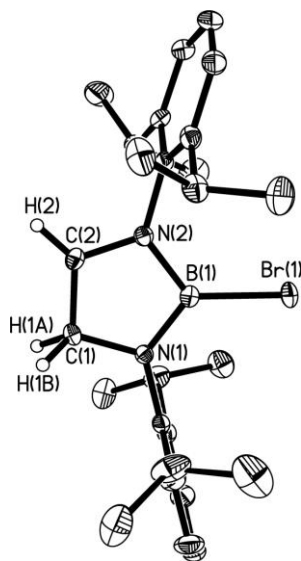


Figure 33. Molecular structure of **[89]⁺**. Thermal ellipsoids represent 30% probability; hydrogen atoms except for those residing at C(1) and C(2) are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: C(1)–C(2) 1.469(7), B(1)–Br(1) 1.885(6); N(1)–B(1)–N(2) 106.4(4), N(1)–B(1)–Br(1) 127.5(4).

Boron tribromide and boron triiodide were utilized in prompting a 1,2-hydrogen migration in 2-bromo-1,3,2-diazaborole to give a 1,3,2-diazaborole-derived carbene complex of boron tribromide (**87**) and boron triiodide (**88**), respectively. The dynamic solution equilibrium behavior of **87** and **88** is consistent with both the weak electron-donating capabilities of 2-bromo-1,3,2-diazaborole-derived carbene, supported by our theoretical study, as well as the relative Lewis acidity of the boron trihalides.

CHAPTER 3

CONCLUSION

3.1 Concluding Remarks

The goal of this research project was to investigate N-heterocyclic carbene-stabilized silylenes, as well as 1,3,2-diazaborole-derived carbene complexes of boron. This work was synthetically challenging, but significantly rewarding, as I was able to synthesize several novel silylene species. Additionally, I synthesized 1,3,2-diazaborole-derived carbene complexes of boron trihalides and investigated their dynamic equilibrium in solution. These complexes are important, as they may lead to the discovery of new N-heterocyclic carbenes.

Inspired by our laboratory's report of a carbene-stabilized disilicon(0)-CuCl complex, I investigated the reactivity of carbene-stabilized disilicon(0) with $\text{Fe}(\text{CO})_5$. Reaction of one equivalent of carbene-stabilized disilicon(0) with one equivalent of $\text{Fe}(\text{CO})_5$ at room temperature yields the carbene-stabilized disilicon(0)- $\text{Fe}(\text{CO})_4$ complex (**72**), where one silicon-based electron lone pair coordinates the $\text{Fe}(\text{CO})_4$ moiety. It is of note that the 1:1 complex is achieved despite the addition of excess $\text{Fe}(\text{CO})_5$ at room temperature, likely due to the steric bulkiness of the carbene ligands. In contrast with the carbene-stabilized disilicon(0)-CuCl complex, the larger steric size of the $\text{Fe}(\text{CO})_4$ unit also likely prevents fluctuation, as no dynamic equilibrium is observed for **72** in solution. Reaction of **72** with an additional equivalent of $\text{Fe}(\text{CO})_5$ at raised temperatures gives carbene-stabilized $\text{Si}[\mu\text{-Fe}_2(\text{CO})_6](\mu\text{-CO})\text{Si}$ (**73**), where the Si=Si double bond present in **72** has been cleaved, and CO and $\text{Fe}_2(\text{CO})_6$ units have been inserted between the silicon atoms. Notably,

compound **73** is the first example of direct Si=Si double bond cleavage by a transition metal species.

Intrigued by the reactivity of **72** with $\text{Fe}(\text{CO})_5$ at raised temperatures to give **73**, I began to explore the reactivity of **72** with other species. Our laboratory has recently reported the synthesis of the carbene-stabilized HP_2^+ cation by reaction of $\text{HCl}\cdot\text{NC}_5\text{H}_5$ with carbene-stabilized diphosphorus. This success inspired me to explore the reactivity of **72** with $\text{HCl}\cdot\text{NC}_5\text{H}_5$. Reaction of one equivalent of **72** with two equivalents of $\text{HCl}\cdot\text{NC}_5\text{H}_5$ yields the “push-pull” stabilized parent monochlorosilylene $[\text{:Si}(\text{H})\text{Cl}]$ (**78**), in which each silylene center accepts a lone pair of electrons from a Lewis basic N-heterocyclic carbene and simultaneously donate an electron lone pair to a central $\text{Fe}(\text{CO})_3$. Compound **78** represents the first experimental stabilization of the parent monochlorosilylene $[\text{:Si}(\text{H})\text{Cl}]$.

Continuing to explore silylene chemistry, we utilized carbene-stabilized bis-silylene to synthesize two new cyclic silylenes containing a silicon-silicon bond. Reaction of bis-silylene (**82**) with two equivalents of thiolate **81** in toluene yields the five-membered cyclic silylene, **83**. Importantly, compound **83** was the first example of “ Si^{I}_2 ” insertion into an olefinic C–H bond. However, when **82** is allowed to react with **81** in THF, a mixture of **83** and a four-membered cyclic silylene **84** is obtained. **84** is formed by silicon(I)-mediated C–N bond cleavage of the N-heterocyclic carbene. Both compounds **83** and **84** are the first cyclic silylenes containing a silicon-silicon bond.

Straying away from silylene chemistry, I began to focus on new main group-initiated carbene formation. Reaction of 2-bromo-1,3,2-diazaborole (**86**) with excess BBr_3 prompts a 1,2-hydrogen shift to give a 1,3,2-diazaborole-derived carbene- BBr_3 complex, **87**. Interestingly, complex **87** is in dynamic equilibrium in solution, likely due to the relatively weak electron-

donating capabilities of the carbene. The approximate molar populations of **86:87** is 2:1 in solution. Reaction of **86** with BI_3 gives the similar 1,3,2-diazaborole-derived carbene- BI_3 complex **88**. In contrast to compound **87**, the equilibrium of **88** in solution largely favors the formation of **88**, with an approximate molar ratio of 1:17 (**86:88**). The large difference in the molar ratios of **86:87** and **86:88** can likely be attributed to the relative Lewis acidity of BI_3 when compared to BBr_3 .

In summary, my research has extended the knowledge base in silylene chemistry, with the first example of transition metal-mediated $\text{Si}=\text{Si}$ double bond cleavage and formation of a silylene center, synthesis of the first parent monochlorosilylene $[\text{:Si(H)Cl}]$, and synthesis of the first example of cyclic silylenes containing a $\text{Si}-\text{Si}$ single bond through unexpected $\text{C}-\text{H}$ and $\text{C}-\text{N}$ bond cleavage. Additionally, I have synthesized 1,3,2-diazaborole-derived carbene- BX_3 ($\text{X} = \text{Br}, \text{I}$) complexes and studied their equilibrium processes. This group continues to study the chemistry of silylenes, as well as 1,3,2-diazaborole-derived carbenes.

CHAPTER 4

EXPERIMENTAL

4.1 General Background

4.1.1 Techniques and Reagents

The syntheses of air-sensitive compounds were performed under purified argon using Schlenk techniques and an inert atmosphere drybox (M-Braun LabMaster SP). Chemicals were purchased from Aldrich and Strem and used as received. The solvents were dried and distilled under argon from Na/benzophenone prior to use. The Schlenk lines were protected under argon, which was first passed through copper-based purification and molecular sieve drying columns prior to use.

4.1.2 Instrumental Measurements

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer, a Bruker Advance III HD 400 MHz spectrometer, or on a Varian Unity Inova 500 MHz spectrometer. ^{29}Si NMR spectra were recorded on a Varian Unity Inova 500 MHz spectrometer, referenced to an external SiMe_4 sample. ^{11}B NMR spectra were recorded on a Bruker Advance III HD 400 MHz spectrometer and a Varian Unity Inova 500 MHz spectrometer, in a quartz NMR tube and referenced to an external BF_3 sample. Infrared spectra were recorded using a Shimadzu IRPrestige-21 FTIR spectrophotometer. Elemental analyses were performed by Complete Analytical Laboratories, Inc. (Highland Park, NJ).

4.1.3 X-ray Diffraction Methods

X-ray quality single crystals were mounted in capillaries in an argon-filled glovebox and sealed with silicon grease before being taken out of the glovebox. The capillaries were flame sealed, and the tip was coated in wax. X-ray intensity data were collected on a Bruker SMART APEX II X-ray diffractometer system with graphite-monochromated Mo K radiation ($\lambda = 0.71073$ Å), using the ω -scan technique or on a Bruker D8 Quest PHOTON 100 CMOS X-ray diffractometer system with Incoatec Microfocus Source (I μ S) monochromated Mo K α radiation ($\lambda = 0.71073$ Å, sealed tube) using phi and omega-scan technique. X-ray intensity data were collected at either room temperature or 100K. All the hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of m Å ($m = 0.950$ for Ph-H groups, $m = 1.000$ for CH groups, $m = 0.990$ for CH₂ groups, $m = 0.980$ for CH₃ groups). Hydrogen atom temperature factors were fixed at n ($n = 1.2$ for CH, CH₂ and Ph-H groups, $n = 1.5$ for CH₃ groups) times the isotropic temperature factor of the C-atom to which they are bonded.

4.2 Preparation of Starting Materials

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

This procedure was performed according to the previously published literature.²⁴¹ A 92% solution of 2,6-diisopropylaniline (322.00 g, 1.67 mol) was measured out and added to a 3000 mL round-bottom flask. The container used to weigh out the 2,6-diisopropylaniline was washed with 2 x 250 mL portions of n-propanol, which was added to the 3000 mL flask. A 40% aqueous solution of glyoxal (109.60 g, 0.76 mol) was added to the 3000 mL flask. The container used to weigh out the glyoxal was washed with 200 mL of n-propanol, which was added to the 3000 mL

flask. 300 mL of water and 1000 mL of n-propanol was added to the 3000 mL reaction flask, and was stirred for 36 hours, giving a bright yellow precipitate. The reaction mixture was filtered and dried *in vacuo* to give the glyoxal-bis-(2,6-diisopropylphenyl)imine. The purity was confirmed by ^1H NMR.

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

This reaction was carried out in the fume hood according to the published procedure.²⁴¹ 1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride (234.68 g, 0.62 mol) was added to a 3000 mL roundbottom flask and dissolved in 1200 mL THF and 6 mL water. A 96% solution of chloromethylethyl ether (69.98g, 0.70 mol) was added to the reaction flask and the mixture was allowed to stir for 16 hours. The reaction mixture was filtered, and the white precipitate of 1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride was washed with THF. The purity was confirmed by ^1H NMR.

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

1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride (20.00 g, 51.47 mmol) was dried *in vacuo* in a Schlenk flask for 36 hours. The white solid was transferred to the glovebox and combined with potassium tert-butoxide (5.81 g, 51.78 mmol) in a 250 mL Schlenk flask. The reaction vessel was brought out of the glovebox and placed under an argon atmosphere on the Schlenk line. 100 mL of dry THF was injected to the reaction vessel and the mixture was stirred for 16 hours. The solvent was evaporated *in vacuo* and the residue was dissolved in 150 mL of dry toluene. The mixture was heated until all the solid dissolved, and the solution was passed through

a bed of celite. The toluene was removed *in vacuo*, giving a pale yellow solid. The purity was confirmed by ^1H NMR.

4.2.4 Synthesis of Potassium Graphite

Graphite flakes (28.00 g, 2.33 mol) were dried in a 220 °C oven for 24 hours and introduced into the glovebox. Potassium metal (11.40 g, 0.29 mol) was cut into small pieces in the glovebox and combined in a high-pressure tube with the graphite flakes and sealed tightly. The reaction tube was brought out of the glovebox and heated with a heat gun while simultaneously being shaken vigorously until the mixture produced a uniform, golden flaky texture, with no remaining potassium or graphite visible in the reaction vessel (quantitative yield).

4.2.5 Synthesis of $L:\text{SiCl}_4$ Complex ($L = \text{C}\{\text{N}(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3)\text{CH}\}_2$)

The synthesis was carried out according to the reported procedure.³⁶ 1,3-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene (15.00 g, 38.60 mmol) was added to 180 mL of hexane in the glovebox. The mixture was stirred until a uniform slurry was achieved (about 20 minutes). SiCl_4 (6.59 g, 38.79 mmol) was added to the slurry slowly, and the reaction mixture was stirred for 16 hours. The solvent was removed *in vacuo*, giving a white solid. The purity was confirmed by ^1H NMR.

4.2.6 Synthesis of Carbene-Stabilized Disilicon(0)

$L:\text{SiCl}_4$ complex (6.00 g, 10.74 mmol) was combined in a 100 mL Schlenk flask with potassium graphite (6.24 g, 46.16 mmol). This was done in four individual Schlenk flasks. All four flasks were brought out of the glovebox and placed on the Schlenk line under argon. 75 mL of dry

THF was injected into each flask, and all four flasks were stirred vigorously for 14 hours. Stirring was stopped after 14 hours, and the reaction mixture was allowed to settle for 2 hours. The THF solution in each 100 mL was separated from the graphite mixture, and all four flasks were filtered into a 500 mL Schlenk flask. The solvent was removed *in vacuo*, and the dark red solid was washed with 3x200 mL of hexane. The solid was dried under vacuum, and the dusty red solid was recrystallized in a concentrated solution of THF. The purity of the crystals was confirmed by ^1H NMR.

4.3 Synthesis of $\text{Fe}(\text{CO})_4$ -Modified Carbene-Stabilized Disilicon(0) Derivatives

4.3.1 Synthesis of $\text{Fe}(\text{CO})_4$ -Modified Carbene-Stabilized Disilicon(0) (**72**)

A 40 mL Schlenk tube was charged with crystals of **2** (0.33 g, 0.40 mmol) and 15 mL of toluene. The mixture was stirred at room temperature until to give a homogeneous dark red solution. $\text{Fe}(\text{CO})_5$ (0.08 g, 0.41 mmol) was added slowly in the reaction system that was then stirred overnight, giving a purple solution. Dark purple crystalline powder of **72** was resulted after removing volatile materials *in vacuo* (0.30 g, 81.0% yield). Mp: melt and decomposed at 217-218 °C. X-ray quality crystals of **72** were obtained by diffusion of hexane into the THF solution of **72**. ^1H NMR (500 MHz, THF-d_8): δ 0.96 [d, 12H, $\text{CH}(\text{CH}_3)_2$], 0.99 [d, 12H, $\text{CH}(\text{CH}_3)_2$], 1.17 [d, 12H, $\text{CH}(\text{CH}_3)_2$], 1.28 [d, 12H, $\text{CH}(\text{CH}_3)_2$], 2.96 [m, 8H, $\text{CH}(\text{CH}_3)_2$], 6.99 [d, 4H, Ar-*H*], 7.16 [d, 4H, Ar-*H*], 7.21 [t, 2H, Ar-*H*], 7.27 [s, 2H, NCH], 7.36 [t, 2H, Ar-*H*], 7.39 [s, 2H, NCH]. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, THF-d_8): δ 23.6 [$\text{CH}(\text{CH}_3)_2$], 23.9 [$\text{CH}(\text{CH}_3)_2$], 26.2 [$\text{CH}(\text{CH}_3)_2$], 26.7 [$\text{CH}(\text{CH}_3)_2$], 29.4 [$\text{CH}(\text{CH}_3)_2$], 125.1, 125.2 (NCH), 126.3, 126.8 (C, *m*-Ar), 130.5, 131.0 (C, *p*-Ar), 136.5, 136.6 (C, *ipso*-Ar), 146.3, 146.6 (C, *o*-Ar), 174.6, 183.0 (NCN), 218.7 (CO). ^{29}Si NMR (THF-d_8 , 99.30 MHz): δ 142.5 and 201.3. IR: $\nu(\text{CO}_{\text{terminal}})$: 1994, 1910, 1896, 1883 cm^{-1} . Crystal data for **2**:

$C_{58}H_{72}FeN_4O_4Si_2$, fw = 1001.22, monoclinic, $P2_1/n$, $a = 11.0073(15)$ Å, $b = 26.776(4)$ Å, $c = 18.990(3)$ Å, $\beta = 95.819(2)^\circ$, $V = 5568.2(13)$ Å³, $Z = 4$, $R1 = 0.0557$ for 6485 data ($I > 2\sigma(I)$), $wR2 = 0.1573$ (all data).

4.3.2 Synthesis of Carbene-Stabilized $Si[\mu-Fe_2(CO)_6](\mu-CO)Si$ (**73**)

A 40 mL Schlenk tube was charged with crystals of **72** (0.26 g, 0.26 mmol) and 15 mL of toluene, which was stirred at room temperature for 10 min. After $Fe(CO)_5$ (0.05 g, 0.26 mmol) was added in the reaction system, the Schlenk tube was placed in a 100°C oil bath and stirred overnight, resulting in a dark orange solution. Orange crystalline powder of **73** was obtained after removing volatile materials *in vacuo* (0.19 g, 97.1% yield). Mp: melt and decomposed at 272-273°C. X-ray quality crystals of **73** were obtained either from the parent toluene solution or by diffusion of hexane into THF solution of **73**. ¹H NMR (400 MHz, THF-d₈): δ 1.02 [d, 24H, $CH(CH_3)_2$], 1.28 [d, 24H, $CH(CH_3)_2$], 2.82 [m, 8H, $CH(CH_3)_2$], 7.20 (d, 8H, Ar-H), 7.33 (t, 4H, Ar-H), 7.67 (s, 4H, NCH). ¹³C{¹H} NMR (100 MHz, THF-d₈): δ 23.3 [$CH(CH_3)_2$], 26.7 [$CH(CH_3)_2$], 29.9 [$CH(CH_3)_2$], 125.5 (NCH), 128.5 (C, *m*-Ar), 131.1 (C, *p*-Ar), 135.5 (C, *ipso*-Ar), 146.1 (C, *o*-Ar), 163.3 (NCN), 221.1 ($CO_{terminal}$), 247.5 ($CO_{bridging}$). ²⁹Si NMR (THF-d₈, 99.30 MHz): δ 109.4. IR: $\nu(CO_{terminal})$: 1991, 1946, 1902, 1890 cm⁻¹; $\nu(CO_{bridging})$: 1628 cm⁻¹. Crystal data for **3**: $C_{68}H_{80}Fe_2N_4O_7Si_2$, fw = 1233.24, orthorhombic, $Pnma$, $a = 20.9033(10)$ Å, $b = 21.8404(10)$ Å, $c = 14.8789(7)$ Å, $V = 6792.8(6)$ Å³, $Z = 4$, $R1 = 0.0524$ for 5599 data ($I > 2\sigma(I)$), $wR2 = 0.1698$ (all data).

4.4 Synthesis of the Parent Monochlorosilylene [:Si(H)Cl]

70 mL of toluene was added to a 100 mL Schlenk flask containing both purple crystals of **72** (1.04 g, 1.04 mmol) and colorless crystals of pyridine hydrochloride (0.24 g, 2.08 mmol) at -78 °C, which was stirred and allowed to gradually warm to room temperature overnight. The orange mixture was then stirred at room temperature for two more hours and filtered. Removing volatile materials from the filtrate *in vacuo* gave compound **7** as orange powder (0.63 g, 58.0% yield). Mp: > 95 °C (gradually decomposed). X-ray quality orange-color crystals of **78**·(**toluene**)₂ were obtained by recrystallization of **78** in toluene. ¹H NMR (499.8 MHz, C₆D₆): δ 0.92-0.95 [m, 24H, CH(CH₃)₂], 1.49-1.59 [m, 24H, CH(CH₃)₂], 2.90-2.96 [m, 4H, CH(CH₃)₂], 3.01-3.08 [m, 4H, CH(CH₃)₂], 6.20, 6.22 (two singlets in a 1:2 ratio, ¹J_{Si-H} = 192 Hz (av.) based on ²⁹Si satellites, 2H, Si-H], 6.34, 6.35 (two singlets in a 2:1 ratio, 4H, NCH), 7.09-7.19 (m, 12H, Ar-H). ¹³C{¹H} NMR (125.7 MHz, THF-d₈): δ 23.42, 23.52, 23.53, 26.37, 26.41, 26.44, 26.52 [CH(CH₃)₂], 29.57, 29.61, 29.69, 29.71 [CH(CH₃)₂], 124.74, 124.86 (NCH), 124.96, 125.0, 126.21, 126.75, 126.80, 129.08, 129.84, 131.38, 131.39, 135.29, 135.38, 138.60, 146.76, 146.80, 146.85 (Ar-C), 164.67, 164.95 (NCN), 216.21, 216.48 (CO). ²⁹Si NMR (C₆D₆, 99.3 MHz): δ 44.02, 45.32 (¹J_{Si-H} = 195 Hz, av.). IR (KBr): ν (CO, cm⁻¹): 1823(s), 1832(s), 1856(br, s), 1934(m), 1941(m); ν (Si-H, cm⁻¹): 2103(m). Crystal data for **78**·(**toluene**)₂: C₇₁H₉₀Cl₂FeN₄O₃Si₂, fw = 1230.39, monoclinic, *P*2₁/*c*, *a* = 19.251(3) Å, *b* = 16.018(2) Å, *c* = 21.996(3) Å, β = 92.636(2)°, *V* = 6775.9(17) Å³, *Z* = 4, *R*₁ = 0.0701 for 8466 data (*I* > 2σ(*I*)), w*R*₂ = 0.2162 (all data).

4.5 Synthesis of Cyclic Silylenes Containing a Silicon-Silicon Bond

4.5.1 Synthesis of Compound **83**

Synthesis of compound **83** in toluene: 6 mL of toluene was added to a Schlenk tube containing both **81** (0.316 g, 0.47 mmol) and **82** (0.252 g, 0.23 mmol) at room temperature. The resulting dark reddish-brown solution was kept stationary in the Schlenk tube over three days, resulting in crystallization of **83**·(toluene)_{2.5}. X-ray quality yellow crystals of **83**·(toluene)_{2.5} (0.192 g, 52.5% yield) was isolated after solvent removal. Characterization of **83**: Mp: gradually decomposed (> 125°C). ¹H NMR (400.14 MHz, THF-d₈): δ 0.55 [d, 3H, CH(CH₃)₂], 0.87-1.32 [multiple d, 66H, CH(CH₃)₂], 1.47 [d, 3H, CH(CH₃)₂], 1.87 [m, 1H, CH(CH₃)₂], 2.16 [m, 1H, CH(CH₃)₂], 2.42 [m, 1H, CH(CH₃)₂], 2.55 [m, 1H, CH(CH₃)₂], 2.70 [m, 6H, CH(CH₃)₂], 2.78 [m, 1H, CH(CH₃)₂], 3.08 [m, 1H, CH(CH₃)₂], 4.61 (s, 1H, Si-H, ¹J_{Si-H} = 196 Hz and ²J_{Si-H} = 20 Hz based on ²⁹Si satellites), 6.30 (s, 1H, SC=CH), 6.97-7.55 (m, 18H, Ar-H), 8.02 (d, 2H, HC=CH). ¹³C{¹H} NMR (100.63 MHz, THF-d₈): δ 22.0, 22.4, 23.29, 23.36, 23.40, 23.6, 24.0, 24.6, 24.8, 24.97, 26.08, 26.2, 26.9 [CH(CH₃)₂], 29.21, 29.50, 29.58, 29.68, 29.72, 29.83, 29.92, 29.95, 30.13, 30.71 [CH(CH₃)₂], 114.6, 123.90, 123.98, 124.09, 124.16, 124.60, 124.64, 124.8, 125.0, 125.1, 125.4, 126.2, 128.1, 129.1, 129.8, 129.9, 130.0, 130.1, 132.6, 132.8, 133.1, 135.0, 135.6, 136.0, 137.8, 138.2, 143.2, 146.9, 147.1, 147.6, 147.78, 147.83, 148.4, 149.0, 156.6, 167.6, 168.8 (imidazole-C and Ar-C). ²⁹Si NMR (THF-d₈, 99.3 MHz): δ -27.00 (¹J_{Si-H} = 195 Hz), -72.98 (²J_{Si-H} = 20 Hz). IR (KBr): ν (Si-H, cm⁻¹): 2109(w). Crystal data for **83**·(toluene)_{2.5}: C_{98.5}H₁₂₆N₆S₄Si₂, fw = 1578.47, monoclinic, C2/c, *a* = 54.583(4) Å, *b* = 14.5630(12) Å, *c* = 25.285(2) Å, *V* = 18791(3) Å³, *Z* = 4, R₁ = 0.0997 for 10627 data (*I* > 2σ(*I*)), wR₂ = 0.2499 (all data).

4.5.2 Synthesis of Compound **84**

Synthesis of compound **83** and **84** in THF: 4 mL of THF was added to a Schlenk tube containing both **81** (0.297 g, 0.44 mmol) and **82** (0.252 g, 0.22 mmol) at room temperature. The resulting dark reddish-brown solution was then stirred at room temperature over one day. After THF removal, the residue was dissolved in 4 mL of toluene and kept at room temperature over two days. Yellow crystals of **83**·(**toluene**)_{2.5} (0.148 g, 42.7%) were isolated after toluene removal. Addition of hexane (1 mL) to the toluene filtrate induced crystallization of **84**·(**toluene**)₂ as colorless crystals (0.021 g, 6.2%, in terms of ¹H NMR data, which shows a 7:1 molar ratio of **83** to **84**). Characterization of **84**: ¹H NMR (400.14 MHz, THF-d₈): δ 0.62 [d, 3H, CH(CH₃)₂], 0.83 [d, 6H, CH(CH₃)₂], 0.90 [d, 3H, CH(CH₃)₂], 1.02-1.33 [multiple d, 60H, CH(CH₃)₂], 2.12 [m, 1H, CH(CH₃)₂], 2.45-2.86 [multiple m, 9H, CH(CH₃)₂], 3.28 [br, 2H, CH(CH₃)₂], 5.20 (s, 1H, SC=CH), 6.16 (s, 1H, SC=CH), 6.94-7.44 (m, 18H, Ar-H), 7.58 (d, 1H, HC=CH), 7.64 (d, 1H, HC=CH). ¹³C{¹H} NMR (100.63 MHz, THF-d₈): δ 22.0, 24.05, 24.09, 24.15, 24.20, 24.27, 24.41, 24.45, 24.53, 24.54, 24.59, 24.92 [CH(CH₃)₂], 29.53, 29.55, 29.72, 29.75, 29.77, 29.83, 29.86, 29.90, 30.2, 30.3 [CH(CH₃)₂], 117.0, 121.2, 121.9, 124.0, 124.33, 124.39, 124.48, 124.52, 124.56, 124.74, 124.87, 124.93, 125.2, 125.3, 125.4, 130.1, 130.27, 130.33, 130.5, 130.7, 131.0, 131.3, 132.7, 133.1, 133.6, 134.4, 135.5, 135.6, 146.7, 147.41, 147.44, 147.48, 147.52, 148.08, 148.12, 148.2, 148.3, 148.5, 167.5, 168.2, 175.6 (imidazole-C and Ar-C). ²⁹Si NMR (THF-d₈, 99.3 MHz): δ 2.21, -56.73. Crystal data for **84**·(**toluene**)₂: C₉₅H₁₂₂N₆S₄Si₂, fw = 1532.40, monoclinic, *P*2₁/*n*, *a* = 17.7211(15) Å, *b* = 27.855(2) Å, *c* = 18.2418(16) Å, β = 92.844(3)°, *V* = 8993.6(13) Å³, *Z* = 4, *R*₁ = 0.0669 for 12920 data (*I* > 2σ(*I*)), *wR*₂ = 0.1883 (all data).

4.6 Synthesis of 1,3,2-Diazaborole-Derived Carbene Complexes of Boron

4.6.1 Synthesis of 1,3,2-Diazaborole-Derived Carbene-BBr₃ Complex

8.9 mL of 1.0 M BBr₃ (in hexanes, 8.90 mmol) solution was added to a Schlenk flask containing **86** (1.037 g, 2.22 mmol) in 25 mL of hexane at room temperature. The mixture was then stirred overnight, giving **87** in a quantitative yield with excess BBr₃ (in terms of the ¹H NMR data). X-ray quality crystals of **87** were observed after crystallization of **87** in the concentrated parent solution at -20 °C overnight. Mp: gradually decomposed (>144°C). ¹H NMR (400.14 MHz, CD₂Cl₂): δ 1.25-1.27 [multiple d, *J* = 4.0 Hz, 12H, CH(CH₃)₂], 1.34 [d, *J* = 4.0 Hz, 6H, CH(CH₃)₂], 1.41 [d, *J* = 4.0 Hz, 6H, CH(CH₃)₂], 2.69 [m, *J* = 8.0 Hz, 2H, CH(CH₃)₂], 2.83 [m, *J* = 8.0 Hz, 2H, CH(CH₃)₂], 5.82 [s, 2H, N-CH₂], 7.28-7.32 [multiple d, *J* = 8.0 Hz, 4H, Ar-*H*], 7.44 [t, *J* = 8.0 Hz, 1H, Ar-*H*], 7.51 [t, *J* = 8.0 Hz, 1H, Ar-*H*]. ¹³C{¹H} NMR (100.63 MHz, CD₂Cl₂): δ 24.22, 24.64, 24.93, 24.99 [CH(CH₃)₂], 29.69, 30.30 [CH(CH₃)₂], 69.88 [NCCH₂], 124.88, 125.17, 130.32, 131.19, 132.85, 133.91, 143.35, 145.79 [Ar-C], 132.61 [NCCH₂]. ¹¹B NMR (C₆D₆, 160.35 MHz): δ For **2**, +30.28 (NBN), -14.42 (CBBr₃); For **86**, +20.10 (NBN); For free BBr₃, +37.14. Anal. (CALI, Highland Park, NJ) Calcd (found) for **87**: C 43.50 (43.48); H 5.06 (5.19); N 3.90 (3.82).

4.6.2 Synthesis of 1,3,2-Diazaborole-Derived Carbene-BI₃ Complex

25 mL of hexane was added to a Schlenk flask containing **86** (1.000 g, 2.14 mmol) and BI₃ (0.922 g, 2.35 mmol) at room temperature. The resulting mixture was stirred overnight, giving **88** in a quantitative yield with excess BI₃ (in terms of the ¹H NMR data). X-ray quality yellow crystals of **88** were observed after recrystallization of **88** in 1,2-difluorobenzene at -20 °C overnight. Mp: 148.2°C. ¹H NMR (400.14 MHz, CD₂Cl₂): δ 1.22-1.26 [multiple d, *J* = 8.0 Hz, 12H, CH(CH₃)₂], 1.31 [d, *J* = 8.0 Hz, 6H, CH(CH₃)₂], 1.45 [d, *J* = 8.0 Hz, 6H, CH(CH₃)₂], 2.72 [m, *J* = 8.0 Hz, 2H,

$\text{CH}(\text{CH}_3)_2$], 2.88 [m, $J = 8.0$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$], 6.42 [s, 2H, N- CH_2], 7.27-7.30 [multiple d, $J = 8.0$ Hz, 4H, Ar- H], 7.42 [t, $J = 8.0$ Hz, 1H, Ar- H], 7.51 [t, $J = 8.0$ Hz, 1H, Ar- H]. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, CD_2Cl_2): δ 24.16, 24.66, 24.74, 24.76 [$\text{CH}(\text{CH}_3)_2$], 29.60, 30.16 [$\text{CH}(\text{CH}_3)_2$], 71.42 [NCCH_2], 125.00, 125.01, 130.12, 131.30, 133.69, 144.24, 145.83 [Ar-C], 132.52 [NCCH_2]. ^{11}B NMR (C_6D_6 , 160.35 MHz): δ For **88**, +30.42 (NBN), -69.52 [CBI_3]; For free BI_3 , -8.07; For **86**, +20.21 (NBN); For the unknown species, +25.26, -45.60. Anal. (CALI, Highland Park, NJ) Calcd (found) for **88**: C 36.36 (35.80); H 4.23 (4.25); N 3.26 (3.07).

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APPENDICES

Table 1. Coordinates of the B3LYP/6-311+G** geometry of **72-Me** optimized in C_1 symmetry.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	14	0	-0.362155	-0.539808	-0.029275
2	14	0	0.872581	-2.361522	0.225079
3	26	0	-0.349398	1.814300	-0.246459
4	7	0	-3.033785	-1.054533	1.137262
5	7	0	-2.850761	-2.038743	-0.775201
6	7	0	3.264637	-0.912999	1.276714
7	7	0	3.434506	-1.258939	-0.847305
8	6	0	-2.167210	-1.267294	0.111770
9	6	0	-4.239326	-1.681065	0.892522
10	1	0	-5.062761	-1.634166	1.583839
11	6	0	-4.124652	-2.302036	-0.307082
12	1	0	-4.828697	-2.899846	-0.859591
13	6	0	-2.360118	-2.494662	-2.075172
14	6	0	-2.739640	-0.259028	2.328818
15	6	0	2.581467	-1.406248	0.205387
16	6	0	4.506872	-0.443061	0.890646
17	1	0	5.195969	0.001373	1.587729
18	6	0	4.612802	-0.658961	-0.443095
19	1	0	5.410182	-0.435100	-1.130316
20	6	0	3.133006	-1.626441	-2.228194
21	6	0	2.751358	-0.851031	2.643872
22	6	0	-2.046045	1.690305	-0.784921
23	8	0	-3.148478	1.612867	-1.133820
24	6	0	0.113272	1.799118	1.474075
25	8	0	0.420152	1.811157	2.594075
26	6	0	-0.319042	3.599520	-0.355104
27	8	0	-0.300055	4.747054	-0.420486
28	6	0	0.906969	1.575587	-1.493406
29	8	0	1.717214	1.446304	-2.310651
30	1	0	4.051469	-1.958887	-2.713506
31	1	0	2.405705	-2.437461	-2.222512
32	1	0	2.714521	-0.772066	-2.761137
33	1	0	2.192016	0.071052	2.804000
34	1	0	2.088027	-1.699074	2.809871
35	1	0	3.593573	-0.901567	3.334726
36	1	0	-1.358029	-2.096281	-2.222241
37	1	0	-2.312001	-3.584306	-2.093974
38	1	0	-3.027642	-2.135159	-2.860468
39	1	0	-2.790463	0.805005	2.096269
40	1	0	-3.468036	-0.508554	3.099534
41	1	0	-1.736580	-0.498913	2.680549

Table 2. Coordinates of the B3LYP/6-311+G** geometry of **73-Me** optimized in C₂ symmetry.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	14	0	-0.094987	1.257592	0.480169
2	14	0	0.094987	-1.257592	0.480169
3	26	0	1.365277	0.104179	-0.903492
4	7	0	-0.540636	4.203680	0.302587
5	6	0	0.000000	3.134401	0.940959
6	6	0	-0.187802	5.371931	0.945209
7	6	0	-1.353052	4.145729	-0.916442
8	6	0	0.000000	-3.134401	0.940959
9	7	0	-0.684603	-3.647321	1.996431
10	6	0	-0.580985	-5.021849	2.008482
11	6	0	-1.487678	-2.868353	2.948825
12	6	0	0.000000	0.000000	1.964095
13	8	0	0.000000	0.000000	3.183951
14	6	0	2.859507	-0.009175	0.024171
15	8	0	3.845230	-0.076172	0.625880
16	6	0	1.599988	-1.031167	-2.257878
17	8	0	1.780111	-1.744136	-3.148604
18	6	0	1.606506	1.633780	-1.775011
19	8	0	1.781916	2.638920	-2.320576
20	26	0	-1.365277	-0.104179	-0.903492
21	7	0	0.684603	3.647321	1.996431
22	6	0	0.580985	5.021849	2.008482
23	6	0	1.487678	2.868353	2.948825
24	7	0	0.540636	-4.203680	0.302587
25	6	0	0.187802	-5.371931	0.945209
26	6	0	1.353052	-4.145729	-0.916442
27	6	0	-2.859507	0.009175	0.024171
28	8	0	-3.845230	0.076172	0.625880
29	6	0	-1.606506	-1.633780	-1.775011
30	8	0	-1.781916	-2.638920	-2.320576
31	6	0	-1.599988	1.031167	-2.257878
32	8	0	-1.780111	1.744136	-3.148604
33	1	0	1.051416	5.625827	2.764815
34	1	0	-0.514019	6.337724	0.600242
35	1	0	0.913375	2.020571	3.322268
36	1	0	1.755864	3.522793	3.776896
37	1	0	2.394804	2.509979	2.459707
38	1	0	-1.884106	5.090805	-1.019066
39	1	0	-0.718246	3.981818	-1.786729
40	1	0	-2.069454	3.331533	-0.834385
41	1	0	-0.913375	-2.020571	3.322268
42	1	0	-2.394804	-2.509979	2.459707
43	1	0	-1.755864	-3.522793	3.776896
44	1	0	1.884106	-5.090805	-1.019066
45	1	0	0.718246	-3.981818	-1.786729
46	1	0	2.069454	-3.331533	-0.834385
47	1	0	0.514019	-6.337724	0.600242
48	1	0	-1.051416	-5.625827	2.764815

Table 3. Sample and crystal data for **72**.

Identification code	72	
Chemical formula	$\text{C}_{58}\text{H}_{72}\text{FeN}_4\text{O}_4\text{Si}_2$	
Formula weight	1001.22 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.070 x 0.190 x 0.340 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 11.0073(15) Å	$\alpha = 90^\circ$
	b = 26.776(4) Å	$\beta = 95.819(2)^\circ$
	c = 18.990(3) Å	$\gamma = 90^\circ$
Volume	5568.2(13) Å ³	
Z	4	
Density (calculated)	1.194 g/cm ³	
Absorption coefficient	0.361 mm ⁻¹	
F(000)	2136	

Table 4. Data collection and structure refinement for **72**.

Theta range for data collection	1.86 to 26.02°	
Index ranges	-13<=h<=13, -33<=k<=33, -23<=l<=23	
Reflections collected	65673	
Independent reflections	10974 [R(int) = 0.1151]	
Max. and min. transmission	0.7454 and 0.5112	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	10974 / 78 / 650	
Goodness-of-fit on F²	1.012	
Final R indices	6485 data; I>2σ(I)	R1 = 0.0557, wR2 = 0.1284
	all data	R1 = 0.1109, wR2 = 0.1573
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0762P) ²] where P=(F _o ² +2F _c ²)/3	
Largest diff. peak and hole	0.397 and -0.391 eÅ ⁻³	
R.M.S. deviation from mean	0.055 eÅ ⁻³	

Table 5. Bond lengths (Å) for **72**.

Si1-C1	1.942(3)	Si1-Si2	2.1951(12)
Si1-Fe1	2.3265(10)	Si2-C28	1.940(3)
Fe1-C55	1.759(4)	Fe1-C57	1.753(4)
Fe1-C58	1.764(4)	Fe1-C56	1.763(4)
N1-C1	1.376(4)	N1-C2	1.374(4)
N1-C16	1.455(4)	N2-C1	1.369(3)
N2-C3	1.380(4)	N2-C4	1.455(4)
N3-C28	1.364(4)	N3-C29	1.393(4)
N3-C43	1.455(4)	N4-C28	1.371(4)
N4-C30	1.385(4)	N4-C31	1.445(4)
C2-C3	1.338(4)	C4-C9	1.389(4)
C4-C5	1.389(4)	C5-C6	1.383(5)
C5-C13	1.529(4)	C6-C7	1.374(5)
C7-C8	1.368(5)	C8-C9	1.388(4)
C9-C10	1.504(5)	C10-C11	1.523(5)
C10-C12	1.531(5)	C13-C15	1.513(5)
C13-C14	1.528(5)	C16-C17	1.394(4)
C16-C21	1.403(4)	C17-C18	1.402(5)
C17-C25	1.509(5)	C18-C19	1.359(5)
C19-C20	1.370(5)	C20-C21	1.391(5)
C21-C22	1.509(5)	C22-C24	1.528(5)
C22-C23	1.527(5)	C25-C26	1.515(5)
C25-C27	1.507(5)	C29-C30	1.325(5)
C31-C32	1.401(5)	C31-C36	1.391(5)
C32-C33	1.384(5)	C32-C40	1.503(6)
C33-C34	1.358(6)	C34-C35	1.375(6)
C35-C36	1.394(5)	C36-C37	1.497(10)
C36-C37'	1.497(16)	C37-C38	1.508(12)
C37-C39	1.499(11)	C37'-C38'	1.507(14)
C37'-C39'	1.511(16)	C40-C42	1.518(6)
C40-C41	1.535(6)	C43-C48	1.390(5)
C43-C44	1.397(5)	C44-C45	1.397(6)
C44-C52	1.506(6)	C45-C46	1.352(7)
C46-C47	1.365(7)	C47-C48	1.396(5)
C48-C49	1.506(5)	C49-C51	1.521(5)
C49-C50	1.536(5)	C52-C54	1.530(6)

C52-C53	1.532(5)	C55-O1	1.161(4)
C56-O2	1.156(4)	C57-O3	1.157(4)
C58-O4	1.152(4)		

Table 6. Bond angles (°) for **72**.

C1-Si1-Si2	101.66(9)	C1-Si1-Fe1	113.40(9)
Si2-Si1-Fe1	144.41(5)	C28-Si2-Si1	106.54(10)
C55-Fe1-C57	93.47(17)	C55-Fe1-C58	115.28(15)
C57-Fe1-C58	95.22(17)	C55-Fe1-C56	128.30(16)
C57-Fe1-C56	91.88(17)	C58-Fe1-C56	115.33(17)
C55-Fe1-Si1	86.97(11)	C57-Fe1-Si1	175.98(12)
C58-Fe1-Si1	88.19(11)	C56-Fe1-Si1	84.73(13)
C1-N1-C2	111.4(2)	C1-N1-C16	130.0(2)
C2-N1-C16	117.6(2)	C1-N2-C3	111.3(2)
C1-N2-C4	129.6(2)	C3-N2-C4	118.7(2)
C28-N3-C29	110.3(3)	C28-N3-C43	128.4(3)
C29-N3-C43	120.5(3)	C28-N4-C30	111.3(3)
C28-N4-C31	126.2(2)	C30-N4-C31	121.7(3)
N2-C1-N1	103.0(2)	N2-C1-Si1	129.3(2)
N1-C1-Si1	127.4(2)	C3-C2-N1	107.1(3)
C2-C3-N2	107.1(3)	C9-C4-C5	123.5(3)
C9-C4-N2	118.7(3)	C5-C4-N2	117.4(3)
C6-C5-C4	117.2(3)	C6-C5-C13	119.6(3)
C4-C5-C13	123.2(3)	C5-C6-C7	120.9(3)
C8-C7-C6	120.4(3)	C7-C8-C9	121.6(3)
C4-C9-C8	116.3(3)	C4-C9-C10	123.7(3)
C8-C9-C10	119.9(3)	C9-C10-C11	111.0(3)
C9-C10-C12	111.6(3)	C11-C10-C12	109.7(3)
C5-C13-C15	113.6(3)	C5-C13-C14	110.3(3)
C15-C13-C14	109.9(3)	C17-C16-C21	123.7(3)
C17-C16-N1	118.2(3)	C21-C16-N1	117.3(3)
C16-C17-C18	116.1(3)	C16-C17-C25	123.9(3)
C18-C17-C25	120.0(3)	C19-C18-C17	121.7(4)
C18-C19-C20	120.7(4)	C21-C20-C19	121.4(4)
C20-C21-C16	116.4(3)	C20-C21-C22	119.8(3)
C16-C21-C22	123.8(3)	C21-C22-C24	112.2(3)
C21-C22-C23	112.1(3)	C24-C22-C23	109.7(3)
C17-C25-C26	110.1(3)	C17-C25-C27	112.7(3)
C26-C25-C27	111.5(4)	N3-C28-N4	103.7(2)
N3-C28-Si2	131.8(2)	N4-C28-Si2	121.5(2)
C30-C29-N3	108.0(3)	C29-C30-N4	106.6(3)
C32-C31-C36	123.5(3)	C32-C31-N4	117.1(3)

C36-C31-N4	119.3(3)	C31-C32-C33	116.7(4)
C31-C32-C40	123.4(3)	C33-C32-C40	119.9(4)
C34-C33-C32	121.5(4)	C33-C34-C35	120.8(4)
C34-C35-C36	121.2(4)	C31-C36-C35	116.3(4)
C31-C36-C37	124.2(7)	C35-C36-C37	119.4(7)
C31-C36-C37'	120.8(10)	C35-C36-C37'	122.7(10)
C36-C37-C38	111.8(12)	C36-C37-C39	115.7(9)
C38-C37-C39	109.4(9)	C36-C37'-C38'	120.0(17)
C36-C37'-C39'	109.6(16)	C38'-C37'-C39'	108.6(15)
C32-C40-C42	112.6(4)	C32-C40-C41	111.4(4)
C42-C40-C41	110.1(4)	C48-C43-C44	123.5(3)
C48-C43-N3	118.6(3)	C44-C43-N3	117.6(3)
C43-C44-C45	116.6(4)	C43-C44-C52	122.4(4)
C45-C44-C52	120.8(4)	C46-C45-C44	121.2(5)
C47-C46-C45	120.9(4)	C46-C47-C48	121.6(5)
C43-C48-C47	116.1(4)	C43-C48-C49	123.8(3)
C47-C48-C49	119.9(4)	C48-C49-C51	114.3(4)
C48-C49-C50	110.0(3)	C51-C49-C50	108.5(3)
C44-C52-C54	111.1(4)	C44-C52-C53	114.3(4)
C54-C52-C53	111.3(4)	O1-C55-Fe1	176.5(3)
O2-C56-Fe1	175.3(3)	O3-C57-Fe1	179.0(4)
O4-C58-Fe1	175.7(3)		

Table 7. Torsion angles (°) for **72**.

C3-N2-C1-N1	1.6(3)	C4-N2-C1-N1	-171.0(3)
C3-N2-C1-Si1	-172.6(2)	C4-N2-C1-Si1	14.9(4)
C2-N1-C1-N2	-0.9(3)	C16-N1-C1-N2	167.6(3)
C2-N1-C1-Si1	173.4(2)	C16-N1-C1-Si1	-18.1(4)
C1-N1-C2-C3	-0.2(4)	C16-N1-C2-C3	-170.2(3)
N1-C2-C3-N2	1.1(4)	C1-N2-C3-C2	-1.8(4)
C4-N2-C3-C2	171.7(3)	C1-N2-C4-C9	-90.4(4)
C3-N2-C4-C9	97.5(3)	C1-N2-C4-C5	96.1(4)
C3-N2-C4-C5	-76.0(4)	C9-C4-C5-C6	2.5(5)
N2-C4-C5-C6	175.6(3)	C9-C4-C5-C13	-175.7(3)
N2-C4-C5-C13	-2.5(4)	C4-C5-C6-C7	-0.3(5)
C13-C5-C6-C7	177.9(3)	C5-C6-C7-C8	-0.9(6)
C6-C7-C8-C9	0.2(6)	C5-C4-C9-C8	-3.2(5)
N2-C4-C9-C8	-176.2(3)	C5-C4-C9-C10	176.2(3)
N2-C4-C9-C10	3.1(5)	C7-C8-C9-C4	1.8(6)
C7-C8-C9-C10	-177.6(4)	C4-C9-C10-C11	112.9(4)
C8-C9-C10-C11	-67.8(4)	C4-C9-C10-C12	-124.4(4)
C8-C9-C10-C12	55.0(4)	C6-C5-C13-C15	47.1(4)
C4-C5-C13-C15	-134.8(4)	C6-C5-C13-C14	-76.8(4)
C4-C5-C13-C14	101.3(4)	C1-N1-C16-C17	-70.2(4)
C2-N1-C16-C17	97.7(3)	C1-N1-C16-C21	119.7(3)
C2-N1-C16-C21	-72.4(4)	C21-C16-C17-C18	0.3(5)
N1-C16-C17-C18	-169.1(3)	C21-C16-C17-C25	176.9(3)
N1-C16-C17-C25	7.5(4)	C16-C17-C18-C19	1.0(5)
C25-C17-C18-C19	-175.8(3)	C17-C18-C19-C20	-1.4(6)
C18-C19-C20-C21	0.4(6)	C19-C20-C21-C16	0.8(5)
C19-C20-C21-C22	179.4(3)	C17-C16-C21-C20	-1.2(5)
N1-C16-C21-C20	168.3(3)	C17-C16-C21-C22	-179.7(3)
N1-C16-C21-C22	-10.2(4)	C20-C21-C22-C24	-74.2(4)
C16-C21-C22-C24	104.3(4)	C20-C21-C22-C23	49.8(4)
C16-C21-C22-C23	-131.8(3)	C16-C17-C25-C26	-95.7(4)
C18-C17-C25-C26	80.8(4)	C16-C17-C25-C27	139.0(4)
C18-C17-C25-C27	-44.4(5)	C29-N3-C28-N4	-0.5(3)
C43-N3-C28-N4	-170.5(3)	C29-N3-C28-Si2	159.8(3)
C43-N3-C28-Si2	-10.2(5)	C30-N4-C28-N3	0.5(3)
C31-N4-C28-N3	170.5(3)	C30-N4-C28-Si2	-162.3(2)
C31-N4-C28-Si2	7.6(4)	C28-N3-C29-C30	0.3(4)

C43-N3-C29-C30	171.2(3)	N3-C29-C30-N4	0.1(4)
C28-N4-C30-C29	-0.4(4)	C31-N4-C30-C29	-170.9(3)
C28-N4-C31-C32	-85.8(4)	C30-N4-C31-C32	83.2(4)
C28-N4-C31-C36	97.9(4)	C30-N4-C31-C36	-93.1(4)
C36-C31-C32-C33	-2.9(5)	N4-C31-C32-C33	-179.0(3)
C36-C31-C32-C40	175.1(3)	N4-C31-C32-C40	-1.1(5)
C31-C32-C33-C34	0.5(6)	C40-C32-C33-C34	-177.5(4)
C32-C33-C34-C35	1.5(8)	C33-C34-C35-C36	-1.4(7)
C32-C31-C36-C35	3.0(5)	N4-C31-C36-C35	179.0(3)
C32-C31-C36-C37	-176.1(5)	N4-C31-C36-C37	-0.1(6)
C32-C31-C36-C37'	-171.9(8)	N4-C31-C36-C37'	4.2(9)
C34-C35-C36-C31	-0.8(6)	C34-C35-C36-C37	178.3(5)
C34-C35-C36-C37'	173.9(9)	C31-C36-C37-C38	-165.5(10)
C35-C36-C37-C38	15.5(13)	C31-C36-C37-C39	68.4(16)
C35-C36-C37-C39	-110.7(15)	C31-C36-C37'-C38'	-135.(2)
C35-C36-C37'-C38'	50.(3)	C31-C36-C37'-C39'	98.(2)
C35-C36-C37'-C39'	-76.(2)	C31-C32-C40-C42	132.9(4)
C33-C32-C40-C42	-49.3(5)	C31-C32-C40-C41	-103.0(5)
C33-C32-C40-C41	74.9(5)	C28-N3-C43-C48	-114.4(4)
C29-N3-C43-C48	76.5(4)	C28-N3-C43-C44	72.3(4)
C29-N3-C43-C44	-96.8(4)	C48-C43-C44-C45	2.2(6)
N3-C43-C44-C45	175.2(3)	C48-C43-C44-C52	-173.0(3)
N3-C43-C44-C52	0.0(5)	C43-C44-C45-C46	-1.3(7)
C52-C44-C45-C46	174.0(4)	C44-C45-C46-C47	0.1(8)
C45-C46-C47-C48	0.2(8)	C44-C43-C48-C47	-1.9(6)
N3-C43-C48-C47	-174.8(3)	C44-C43-C48-C49	173.8(3)
N3-C43-C48-C49	0.9(5)	C46-C47-C48-C43	0.6(7)
C46-C47-C48-C49	-175.2(4)	C43-C48-C49-C51	136.4(4)
C47-C48-C49-C51	-48.0(5)	C43-C48-C49-C50	-101.2(4)
C47-C48-C49-C50	74.3(5)	C43-C44-C52-C54	88.0(5)
C45-C44-C52-C54	-87.0(5)	C43-C44-C52-C53	-145.1(4)
C45-C44-C52-C53	40.0(5)		

Table 8. Sample and crystal data for **73**.

Identification code	73	
Chemical formula	$\text{C}_{68}\text{H}_{80}\text{Fe}_2\text{N}_4\text{O}_7\text{Si}_2$	
Formula weight	1233.24 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.120 x 0.320 x 0.550 mm	
Crystal system	orthorhombic	
Space group	P n m a	
Unit cell dimensions	a = 20.9033(10) Å	$\alpha = 90^\circ$
	b = 21.8404(10) Å	$\beta = 90^\circ$
	c = 14.8789(7) Å	$\gamma = 90^\circ$
Volume	6792.8(6) Å ³	
Z	4	
Density (calculated)	1.206 g/cm ³	
Absorption coefficient	0.515 mm ⁻¹	
F(000)	2608	

Table 9. Data collection and structure refinement for **73**.

Theta range for data collection	1.92 to 27.88°
Index ranges	-27<= <i>h</i> <=27, -28<= <i>k</i> <=28, -19<= <i>l</i> <=19
Reflections collected	89925
Independent reflections	8318 [R(int) = 0.0399]
Max. and min. transmission	0.7457 and 0.6170
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	8318 / 476 / 508
Goodness-of-fit on F²	1.053
$\Delta/\sigma_{\max}$	0.001
Final R indices	5599 data; R1 = 0.0524, wR2 = I>2σ(I) 0.1397 all data R1 = 0.0831, wR2 = 0.1698
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0795P)^2+3.0171P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.507 and -0.269 eÅ ⁻³
R.M.S. deviation from mean	0.050 eÅ ⁻³

Table 10. Bond lengths (Å) for **73**.

Si1-C1	1.933(3)	Si1-C29	1.957(3)
Si1-Fe1	2.2867(8)	Si1-Fe1	2.2867(8)
Si1-Si2	2.5206(13)	Si2-C15	1.935(3)
Si2-C29	1.937(4)	Si2-Fe1	2.2930(8)
Si2-Fe1	2.2930(8)	Fe1-C32	1.714(8)
Fe1-C31A	1.744(10)	Fe1-C30	1.751(4)
Fe1-C31	1.800(8)	Fe1-C32A	1.828(8)
Fe1-Fe1	2.6658(8)	N1-C1	1.358(3)
N1-C2	1.382(3)	N1-C3	1.458(3)
C1-N1	1.358(3)	C2-C2	1.324(6)
C3-C8	1.369(5)	C3-C4	1.406(5)
C4-C5	1.384(6)	C4-C12	1.490(7)
C5-C6	1.313(11)	C6-C7	1.364(11)
C7-C8	1.404(6)	C8-C9	1.518(6)
C9-C11	1.524(6)	C9-C10	1.536(7)
C12-C13	1.531(7)	C12-C14	1.539(7)
C15-N2	1.360(5)	C15-N2	1.360(5)
C15-N2A	1.357(6)	C15-N2A	1.357(6)
N2-C16	1.386(13)	N2-C17	1.406(7)
C17-C18	1.39	C17-C22	1.39
C18-C26	1.539(11)	C18-C19	1.39
C20-C21	1.39	C19-C20	1.39
C21-C22	1.39	C22-C23	1.545(10)
C23-C24	1.540(11)	C23-C25	1.575(11)
C26-C28	1.540(13)	C26-C27	1.539(13)
N2A-C16A	1.376(11)	N2A-C17A	1.406(7)
C17A-C18A	1.39	C17A-C22A	1.39
C18A-C19A	1.39	C18A-C26A	1.591(10)
C19A-C20A	1.39	C20A-C21A	1.39
C21A-C22A	1.39	C22A-C23A	1.487(13)
C23A-C25A	1.548(12)	C23A-C24A	1.559(12)
C26A-C26A	1.507(19)	C26A-C27A	1.549(11)
C26A-C28A	1.550(11)	C29-O1	1.194(4)
C30-O2	1.162(4)	C31-O3	1.165(9)
C31A-O3A	1.139(10)	C32-O4	1.126(8)
C32A-O4A	1.169(8)	C33-C34	1.39

C33-C38	1.39	C34-C35	1.39
C35-C36	1.39	C36-C37	1.39
C37-C38	1.39	C38-C39	1.506(17)

Table 11. Bond angles (°) for **73**.

C1-Si1-C29	114.21(15)	C1-Si1-Fe1	134.11(6)
C29-Si1-Fe1	95.55(10)	C1-Si1-Fe1	134.11(6)
C29-Si1-Fe1	95.56(10)	Fe1-Si1-Fe1	71.31(3)
C1-Si1-Si2	163.52(11)	C29-Si1-Si2	49.31(12)
Fe1-Si1-Si2	56.73(3)	Fe1-Si1-Si2	56.73(3)
C15-Si2-C29	115.76(16)	C15-Si2-Fe1	133.00(8)
C29-Si2-Fe1	95.93(9)	C15-Si2-Fe1	133.00(8)
C29-Si2-Fe1	95.93(9)	Fe1-Si2-Fe1	71.08(3)
C15-Si2-Si1	165.78(13)	C29-Si2-Si1	50.02(11)
Fe1-Si2-Si1	56.49(2)	Fe1-Si2-Si1	56.49(2)
C32-Fe1-C30	95.5(4)	C31A-Fe1-C30	104.3(7)
C32-Fe1-C31	97.2(7)	C30-Fe1-C31	101.9(5)
C31A-Fe1-C32A	91.5(8)	C30-Fe1-C32A	110.3(4)
C32-Fe1-Si1	103.4(5)	C31A-Fe1-Si1	154.3(7)
C30-Fe1-Si1	100.95(11)	C31-Fe1-Si1	147.4(5)
C32A-Fe1-Si1	84.0(4)	C32-Fe1-Si2	161.0(4)
C31A-Fe1-Si2	102.9(6)	C30-Fe1-Si2	102.24(11)
C31-Fe1-Si2	85.9(6)	C32A-Fe1-Si2	139.8(5)
Si1-Fe1-Si2	66.79(3)	C32-Fe1-Fe1	106.5(4)
C31A-Fe1-Fe1	100.2(6)	C30-Fe1-Fe1	149.71(10)
C31-Fe1-Fe1	95.8(5)	C32A-Fe1-Fe1	86.3(5)
Si1-Fe1-Fe1	54.345(16)	Si2-Fe1-Fe1	54.459(16)
C1-N1-C2	110.4(2)	C1-N1-C3	128.7(2)
C2-N1-C3	121.0(2)	N1-C1-N1	104.6(3)
N1-C1-Si1	126.90(14)	N1-C1-Si1	126.90(14)
C2-C2-N1	107.36(15)	C8-C3-C4	124.0(3)
C8-C3-N1	117.9(3)	C4-C3-N1	117.8(3)
C5-C4-C3	114.5(5)	C5-C4-C12	121.7(4)
C3-C4-C12	123.7(3)	C6-C5-C4	124.0(6)
C5-C6-C7	120.5(5)	C6-C7-C8	120.7(6)
C3-C8-C7	116.4(5)	C3-C8-C9	123.1(3)
C7-C8-C9	120.5(5)	C8-C9-C11	114.7(4)
C8-C9-C10	111.6(5)	C11-C9-C10	109.2(4)
C4-C12-C13	111.0(5)	C4-C12-C14	111.8(5)
C13-C12-C14	108.9(4)	N2-C15-N2	83.9(5)
N2A-C15-N2A	86.7(5)	N2-C15-Si2	129.5(3)
N2-C15-Si2	129.5(3)	N2A-C15-Si2	125.9(3)

N2A-C15-Si2	125.9(3)	C15-N2-C16	109.8(7)
C15-N2-C17	130.0(4)	C16-N2-C17	120.3(7)
C15-N2-N2	48.0(3)	C16-N2-N2	73.5(6)
C17-N2-N2	147.4(3)	C15-N2-C16	83.5(5)
C16-N2-C16	30.5(9)	C17-N2-C16	143.6(5)
N2-N2-C16	43.0(4)	C16-C16-N2	106.5(6)
C16-C16-N2	43.0(4)	N2-C16-N2	63.5(6)
C18-C17-C22	120.0	C18-C17-N2	120.0(5)
C22-C17-N2	119.8(5)	C18-C17-C24A	64.6(4)
C22-C17-C24A	82.2(4)	N2-C17-C24A	120.5(5)
C17-C18-C19	120.0	C17-C18-C26	121.9(6)
C19-C18-C26	117.9(6)	C17-C18-C25A	108.6(6)
C19-C18-C25A	20.3(5)	C26-C18-C25A	127.8(8)
C17-C18-C24A	72.6(4)	C19-C18-C24A	77.3(4)
C26-C18-C24A	117.2(8)	C25A-C18-C24A	88.2(6)
C18-C19-C20	120.0	C25A-C20-C19	28.0(7)
C25A-C20-C21	119.5(8)	C19-C20-C21	120.0
C22-C21-C20	120.0	C21-C22-C17	120.0
C21-C22-C23	120.0(5)	C17-C22-C23	119.9(5)
C24-C23-C22	114.8(8)	C24-C23-C25	108.2(8)
C22-C23-C25	111.4(8)	C28-C26-C18	111.8(10)
C28-C26-C27	106.0(10)	C18-C26-C27	118.8(10)
C17A-C28-C22A	47.3(3)	C15-N2A-C16A	110.3(6)
C15-N2A-C17A	129.7(4)	C16A-N2A-C17A	120.0(6)
C15-N2A-N2A	46.7(3)	C16A-N2A-N2A	75.4(6)
C17A-N2A-N2A	146.9(4)	C16A-C16A-N2A	104.6(6)
C18A-C17A-C22A	120.0	C18A-C17A-N2A	119.4(5)
C22A-C17A-N2A	120.4(5)	C18A-C17A-C28	80.5(5)
C22A-C17A-C28	66.6(5)	N2A-C17A-C28	119.3(6)
C17A-C18A-C19A	120.0	C17A-C18A-C26A	119.5(5)
C19A-C18A-C26A	120.3(5)	C20A-C19A-C18A	120.0
C19A-C20A-C21A	120.0	C22A-C21A-C20A	120.0
C21A-C22A-C17A	120.0	C21A-C22A-C23A	118.2(6)
C17A-C22A-C23A	121.5(6)	C21A-C22A-C28	80.9(4)
C17A-C22A-C28	66.1(5)	C23A-C22A-C28	118.9(8)
C22A-C23A-C25A	117.9(10)	C22A-C23A-C24A	114.7(9)
C25A-C23A-C24A	107.5(9)	C18-C24A-C17	42.8(2)
C20-C25A-C18	111.3(10)	C26A-C26A-C27A	86.9(6)

C26A-C26A-C28A	87.2(6)	C27A-C26A-C28A	107.6(8)
C26A-C26A-C18A	147.9(4)	O1-C29-Si2	140.0(3)
O1-C29-Si1	139.3(3)	Si2-C29-Si1	80.67(14)
O2-C30-Fe1	178.6(3)	O3-C31-Fe1	177.7(9)
O3A-C31A-Fe1	176.6(11)	O4-C32-Fe1	173.8(10)
O4A-C32A-Fe1	177.7(8)	C34-C33-C38	120.0
C35-C34-C33	120.0	C34-C35-C36	120.0
C37-C36-C35	120.0	C38-C37-C36	120.0
C37-C38-C33	120.0	C37-C38-C39	98.7(12)
C33-C38-C39	129.8(16)		

Table 12. Torsion angles (°) for **73**.

C2-N1-C1-N1	-1.6(4)	C3-N1-C1-N1	177.8(2)
C2-N1-C1-Si1	164.5(2)	C3-N1-C1-Si1	-16.1(5)
C1-N1-C2-C2	1.0(2)	C3-N1-C2-C2	-178.4(2)
C1-N1-C3-C8	92.7(4)	C2-N1-C3-C8	-87.9(4)
C1-N1-C3-C4	-93.5(4)	C2-N1-C3-C4	85.8(4)
C8-C3-C4-C5	-0.4(5)	N1-C3-C4-C5	-173.8(3)
C8-C3-C4-C12	177.2(4)	N1-C3-C4-C12	3.9(5)
C3-C4-C5-C6	1.0(7)	C12-C4-C5-C6	-176.7(5)
C4-C5-C6-C7	-1.4(10)	C5-C6-C7-C8	1.0(10)
C4-C3-C8-C7	0.1(5)	N1-C3-C8-C7	173.5(3)
C4-C3-C8-C9	-177.7(4)	N1-C3-C8-C9	-4.4(5)
C6-C7-C8-C3	-0.4(7)	C6-C7-C8-C9	177.5(5)
C3-C8-C9-C11	-141.3(4)	C7-C8-C9-C11	40.9(6)
C3-C8-C9-C10	93.8(5)	C7-C8-C9-C10	-84.0(6)
C5-C4-C12-C13	89.7(6)	C3-C4-C12-C13	-87.7(5)
C5-C4-C12-C14	-32.0(6)	C3-C4-C12-C14	150.5(4)
N2-C15-N2-C16	43.2(8)	Si2-C15-N2-C16	-179.0(6)
N2-C15-N2-C17	-136.5(5)	Si2-C15-N2-C17	1.3(9)
Si2-C15-N2-N2	137.7(6)	N2-C15-N2-C16	27.5(5)
Si2-C15-N2-C16	165.2(4)	C15-N2-C16-C16	-32.1(6)
C17-N2-C16-C16	147.6(5)	N2-N2-C16-C16	0.0020(10)
C15-N2-C16-N2	-32.1(6)	C17-N2-C16-N2	147.6(5)
C16-N2-C16-N2	-0.002(2)	C15-N2-C17-C18	-82.9(7)
C16-N2-C17-C18	97.5(8)	N2-N2-C17-C18	-154.9(4)
C16-N2-C17-C18	124.7(9)	C15-N2-C17-C22	101.7(7)
C16-N2-C17-C22	-78.0(8)	N2-N2-C17-C22	29.7(7)
C16-N2-C17-C22	-50.7(11)	C15-N2-C17-C24A	-159.3(6)
C16-N2-C17-C24A	21.1(10)	N2-N2-C17-C24A	128.7(5)
C16-N2-C17-C24A	48.3(12)	C22-C17-C18-C19	0
N2-C17-C18-C19	-175.4(5)	C24A-C17-C18-C19	-63.4(4)
C22-C17-C18-C26	175.1(8)	N2-C17-C18-C26	-0.3(8)
C24A-C17-C18-C26	111.7(9)	C22-C17-C18-C25A	-18.5(5)
N2-C17-C18-C25A	166.0(7)	C24A-C17-C18-C25A	-82.0(7)
C22-C17-C18-C24A	63.4(4)	N2-C17-C18-C24A	-112.0(6)
C17-C18-C19-C20	0	C26-C18-C19-C20	-175.3(8)
C25A-C18-C19-C20	60.1(17)	C24A-C18-C19-C20	-61.0(4)

C18-C19-C20-C25A	-97.3(16)	C18-C19-C20-C21	0
C25A-C20-C21-C22	32.4(8)	C19-C20-C21-C22	0
C20-C21-C22-C17	0	C20-C21-C22-C23	177.0(6)
C18-C17-C22-C21	0	N2-C17-C22-C21	175.5(5)
C24A-C17-C22-C21	54.6(4)	C18-C17-C22-C23	-177.0(6)
N2-C17-C22-C23	-1.5(7)	C24A-C17-C22-C23	-122.4(6)
C21-C22-C23-C24	39.8(8)	C17-C22-C23-C24	-143.2(6)
C21-C22-C23-C25	-83.7(9)	C17-C22-C23-C25	93.3(9)
C17-C18-C26-C28	-74.4(10)	C19-C18-C26-C28	100.8(9)
C25A-C18-C26-C28	122.1(10)	C24A-C18-C26-C28	11.2(12)
C17-C18-C26-C27	161.6(8)	C19-C18-C26-C27	-23.1(12)
C25A-C18-C26-C27	-1.9(15)	C24A-C18-C26-C27	-112.7(10)
N2A-C15-N2A-C16A	-44.0(9)	Si2-C15-N2A-C16A	-177.1(6)
N2A-C15-N2A-C17A	135.6(6)	Si2-C15-N2A-C17A	2.5(10)
Si2-C15-N2A-N2A	-133.1(6)	C15-N2A-C16A-C16A	31.5(6)
C17A-N2A-C16A-C16A	-148.1(6)	N2A-N2A-C16A-C16A	0.004(2)
C15-N2A-C17A-C18A	-97.7(7)	C16A-N2A-C17A-C18A	81.8(9)
N2A-N2A-C17A-C18A	-28.8(7)	C15-N2A-C17A-C22A	88.0(8)
C16A-N2A-C17A-C22A	-92.5(8)	N2A-N2A-C17A-C22A	156.9(4)
C15-N2A-C17A-C28	166.5(7)	C16A-N2A-C17A-C28	-13.9(11)
N2A-N2A-C17A-C28	-124.5(6)	C22A-C28-C17A-C18A	128.6(3)
C22A-C28-C17A-N2A	-112.9(7)	C22A-C17A-C18A-C19A	0
N2A-C17A-C18A-C19A	-174.3(5)	C28-C17A-C18A-C19A	-55.9(5)
C22A-C17A-C18A-C26A	175.7(6)	N2A-C17A-C18A-C26A	1.4(7)
C28-C17A-C18A-C26A	119.8(6)	C17A-C18A-C19A-C20A	0
C26A-C18A-C19A-C20A	-175.7(6)	C18A-C19A-C20A-C21A	0
C19A-C20A-C21A-C22A	0	C20A-C21A-C22A-C17A	0

C20A-C21A-C22A-C23A	173.4(7)	C20A-C21A-C22A-C28	55.5(5)
C18A-C17A-C22A-C21A	0	N2A-C17A-C22A-C21A	174.3(5)
C28-C17A-C22A-C21A	62.9(5)	C18A-C17A-C22A-C23A	-173.2(8)
N2A-C17A-C22A-C23A	1.1(8)	C28-C17A-C22A-C23A	-110.3(9)
C18A-C17A-C22A-C28	-62.9(5)	N2A-C17A-C22A-C28	111.4(6)
C17A-C28-C22A-C21A	-128.7(3)	C17A-C28-C22A-C23A	114.1(8)
C21A-C22A-C23A-C25A	35.6(11)	C17A-C22A-C23A-C25A	-151.0(8)
C28-C22A-C23A-C25A	130.8(9)	C21A-C22A-C23A-C24A	-92.6(9)
C17A-C22A-C23A-C24A	80.7(10)	C28-C22A-C23A-C24A	2.5(12)
C19-C18-C24A-C17	127.4(2)	C26-C18-C24A-C17	-117.5(7)
C25A-C18-C24A-C17	110.1(6)	C19-C20-C25A-C18	47.0(9)
C21-C20-C25A-C18	-52.1(12)	C17-C18-C25A-C20	46.5(12)
C19-C18-C25A-C20	-81.1(17)	C26-C18-C25A-C20	-148.3(11)
C24A-C18-C25A-C20	-24.5(12)	C17A-C18A-C26A-C26A	26.8(9)
C19A-C18A-C26A-C26A	-157.5(5)	C38-C33-C34-C35	0
C33-C34-C35-C36	0	C34-C35-C36-C37	0
C35-C36-C37-C38	0	C36-C37-C38-C33	0
C36-C37-C38-C39	-147.(2)	C34-C33-C38-C37	0
C34-C33-C38-C39	135.(2)		

Table 13. Coordinates of the B3LYP/6-311+G** geometry of **78-H** optimized in C_2 symmetry.

Standard orientation:					
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	26	0	0.000000	0.000000	0.484486
2	14	0	-0.919410	2.026238	0.570452
3	1	0	-1.423464	2.641415	1.834764
4	17	0	-2.530103	2.631404	-0.765410
5	14	0	0.919410	-2.026238	0.570452
6	1	0	1.423464	-2.641415	1.834764
7	17	0	2.530103	-2.631404	-0.765410
8	7	0	0.000000	4.487307	-0.825523
9	7	0	1.555275	3.692392	0.400651
10	7	0	0.000000	-4.487307	-0.825523
11	7	0	-1.555275	-3.692392	0.400651
12	6	0	0.274365	3.489146	0.033981
13	6	0	1.093827	5.312808	-1.007228
14	1	0	1.078536	6.165181	-1.663183
15	6	0	2.082667	4.805333	-0.225830
16	1	0	3.095935	5.131636	-0.069814
17	6	0	-0.274365	-3.489146	0.033981
18	6	0	-1.093827	-5.312808	-1.007228
19	1	0	-1.078536	-6.165181	-1.663183
20	6	0	-2.082667	-4.805333	-0.225830
21	1	0	-3.095935	-5.131636	-0.069814
22	6	0	0.000000	0.000000	-1.295061
23	8	0	0.000000	0.000000	-2.453294
24	6	0	1.375101	0.680834	1.321600
25	8	0	2.275128	1.219986	1.853443
26	6	0	-1.375101	-0.680834	1.321600
27	8	0	-2.275128	-1.219986	1.853443
28	1	0	2.060573	3.047671	1.005937
29	1	0	-0.908261	4.557789	-1.270606
30	1	0	-2.060573	-3.047671	1.005937
31	1	0	0.908261	-4.557789	-1.270606

Table 14. Sample and crystal data for **78·(toluene)₂**.

Identification code	78·(toluene)₂	
Chemical formula	C ₇₁ H ₉₀ Cl ₂ FeN ₄ O ₃ Si ₂	
Formula weight	1230.39 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.220 x 0.350 mm	
Crystal system	monoclinic	
Space group	P2 ₁ /c (No. 14),	
Unit cell dimensions	a = 19.251(3) Å	α = 90°
	b = 16.018(2) Å	β = 92.636(2)°
	c = 21.996(3) Å	γ = 90°
Volume	6775.9(17) Å ³	
Z	4	
Density (calculated)	1.206 g/cm ³	
Absorption coefficient	0.385 mm ⁻¹	
F(000)	2624	

Table 15. Data collection and structure refinement for **78·(toluene)₂**.

Theta range for data collection	1.92 to 25.25°
Index ranges	-23<= <i>h</i> <=23, -19<= <i>k</i> <=19, -26<= <i>l</i> <=26
Reflections collected	74550
Independent reflections	12272 [R(int) = 0.0723]
Max. and min. transmission	0.7457 and 0.5787
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	12272 / 389 / 884
Goodness-of-fit on F²	1.042
Final R indices	8466 data; I>2σ(I) R1 = 0.0701, wR2 = 0.1892 all data R1 = 0.1010, wR2 = 0.2162
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1106P)^2+7.6522P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.912 and -0.479 eÅ ⁻³
R.M.S. deviation from mean	0.070 eÅ ⁻³

Table 16. Bond lengths (Å) for **78·(toluene)₂**.

Fe1-C55	1.764(5)	Fe1-C56	1.748(4)
Fe1-C57	1.742(4)	Fe1-Si2	2.189(3)
Fe1-Si1'	2.219(17)	Fe1-Si1	2.213(3)
Fe1-Si2'	2.280(8)	Fe1-Si2''	2.263(15)
Si1-H1	1.50(2)	Si1-C1	1.955(5)
Si1-Cl1	2.135(5)	Si1'-H1'	1.50(2)
Si1'-C1	1.955(13)	Si1'-Cl1'	2.100(18)
Si2-H2	1.474(19)	Si2-C28	1.957(5)
Si2-Cl2	2.127(3)	Si2'-H2'	1.461(10)
Si2'-C28	1.977(8)	Si2'-Cl2'	2.126(11)
Si2''-H2''	1.553(17)	Si2''-C28	1.960(14)
Si2''-Cl2''	2.121(15)	N1-C1	1.364(5)
N1-C2	1.380(5)	N1-C16	1.452(5)
N2-C1	1.362(5)	N2-C3	1.387(5)
N2-C4	1.465(5)	N3-C29	1.380(5)
N3-C28	1.369(6)	N3-C43	1.461(6)
N4-C28	1.378(5)	N4-C30	1.380(6)
N4-C31	1.489(6)	C2-C3	1.341(6)
C4-C9	1.387(6)	C4-C5	1.388(6)
C5-C6	1.390(7)	C5-C13	1.495(7)
C6-C7	1.360(8)	C7-C8	1.353(8)
C8-C9	1.418(7)	C9-C10	1.506(7)
C10-C11	1.508(8)	C10-C12	1.522(8)
C13-C14	1.532(7)	C13-C15	1.543(9)
C16-C17	1.387(6)	C16-C21	1.413(6)
C17-C18	1.405(6)	C17-C25	1.516(6)
C18-C19	1.376(7)	C19-C20	1.379(7)
C20-C21	1.385(6)	C21-C22	1.506(7)
C22-C24	1.526(7)	C22-C23	1.531(6)
C25-C26	1.523(6)	C25-C27	1.529(6)
C29-C30	1.333(7)	C31-C36	1.400(8)
C31-C32	1.393(7)	C32-C40	1.459(9)
C32-C33	1.449(8)	C33-C34	1.359(9)
C34-C35	1.354(8)	C35-C36	1.399(7)
C36-C37	1.500(8)	C37-C39	1.513(8)
C37-C38	1.525(8)	C40-C41	1.600(9)
C40-C42	1.587(8)	C43-C44	1.392(7)

C43-C48	1.403(7)	C44-C45	1.401(8)
C44-C52	1.499(7)	C45-C46	1.381(8)
C46-C47	1.384(8)	C47-C48	1.395(7)
C48-C49	1.510(7)	C49-C50	1.525(6)
C49-C51	1.532(6)	C52-C54	1.527(7)
C52-C53	1.549(7)	C55-O1	1.155(5)
C56-O2	1.172(5)	C57-O3	1.183(5)
C58-C59	1.295(10)	C58-C63	1.436(12)
C58-C64	1.440(12)	C59-C60	1.426(9)
C60-C61	1.345(9)	C61-C62	1.387(10)
C62-C63	1.364(11)	C65-C66	1.35(2)
C65-C70	1.38(2)	C65-C71	1.490(17)
C66-C67	1.435(17)	C67-C68	1.33(2)
C68-C69	1.350(19)	C69-C70	1.45(2)
C65'-C70'	1.347(17)	C65'-C66'	1.375(18)
C65'-C71'	1.475(16)	C66'-C67'	1.420(17)
C67'-C68'	1.338(18)	C68'-C69'	1.353(16)
C69'-C70'	1.44(2)		

Table 17. Bond angles (°) for **78·(toluene)₂**.

C55-Fe1-C56	120.18(18)	C55-Fe1-C57	122.71(19)
C56-Fe1-C57	117.05(18)	C55-Fe1-Si2	95.49(17)
C56-Fe1-Si2	81.96(15)	C57-Fe1-Si2	89.66(15)
C55-Fe1-Si1'	83.2(8)	C56-Fe1-Si1'	98.0(5)
C57-Fe1-Si1'	91.8(6)	C55-Fe1-Si1	91.7(2)
C56-Fe1-Si1	95.21(16)	C57-Fe1-Si1	85.70(16)
Si2-Fe1-Si1	172.77(18)	C55-Fe1-Si2'	71.6(3)
C56-Fe1-Si2'	95.7(3)	C57-Fe1-Si2'	100.7(2)
Si1'-Fe1-Si2'	154.8(8)	C55-Fe1-Si2''	84.9(6)
C56-Fe1-Si2''	85.6(4)	C57-Fe1-Si2''	97.1(5)
H1-Si1-Cl1	101(2)	H1-Si1-Cl1	100(3)
C1-Si1-Cl1	98.7(2)	H1-Si1-Fe1	117(2)
C1-Si1-Fe1	120.42(18)	Cl1-Si1-Fe1	117.03(19)
H1'-Si1'-C1	101(10)	H1'-Si1'-Cl1'	118(10)
C1-Si1'-Cl1'	95.6(8)	H1'-Si1'-Fe1	102(10)
C1-Si1'-Fe1	120.1(10)	Cl1'-Si1'-Fe1	119.8(11)
H2-Si2-C28	92(2)	H2-Si2-Cl2	97(2)
C28-Si2-Cl2	95.14(18)	H2-Si2-Fe1	125.(2)
C28-Si2-Fe1	122.49(19)	Cl2-Si2-Fe1	117.97(15)
H2'-Si2'-C28	112.3(5)	H2'-Si2'-Cl2'	98.4(5)
C28-Si2'-Cl2'	95.2(4)	H2'-Si2'-Fe1	114.3(5)
C28-Si2'-Fe1	117.2(4)	Cl2'-Si2'-Fe1	116.5(5)
H2''-Si2''-C28	97.1(8)	H2''-Si2''-Cl2''	96.8(19)
C28-Si2''-Cl2''	102.7(9)	H2''-Si2''-Fe1	119.8(11)
C28-Si2''-Fe1	118.7(8)	Cl2''-Si2''-Fe1	117.6(9)
C1-N1-C2	110.5(3)	C1-N1-C16	125.6(3)
C2-N1-C16	123.2(3)	C1-N2-C3	110.6(3)
C1-N2-C4	127.2(3)	C3-N2-C4	121.7(3)
C29-N3-C28	110.6(4)	C29-N3-C43	121.5(4)
C28-N3-C43	127.6(3)	C28-N4-C30	109.9(4)
C28-N4-C31	126.7(4)	C30-N4-C31	123.2(3)
N1-C1-N2	104.6(3)	N1-C1-Si1	130.1(3)
N2-C1-Si1	124.5(3)	N1-C1-Si1'	121.0(8)
N2-C1-Si1'	134.2(9)	C3-C2-N1	107.6(3)
C2-C3-N2	106.7(4)	C9-C4-C5	123.7(4)
C9-C4-N2	117.3(4)	C5-C4-N2	119.0(4)
C4-C5-C6	116.8(5)	C4-C5-C13	122.0(4)

C6-C5-C13	121.2(4)	C7-C6-C5	121.5(5)
C6-C7-C8	120.9(5)	C7-C8-C9	121.1(5)
C4-C9-C8	116.0(4)	C4-C9-C10	123.5(4)
C8-C9-C10	120.4(4)	C9-C10-C11	113.2(4)
C9-C10-C12	111.5(5)	C11-C10-C12	109.4(5)
C5-C13-C14	112.7(5)	C5-C13-C15	109.9(5)
C14-C13-C15	110.9(5)	C17-C16-C21	123.4(4)
C17-C16-N1	119.3(3)	C21-C16-N1	117.3(4)
C16-C17-C18	116.8(4)	C16-C17-C25	122.7(4)
C18-C17-C25	120.4(4)	C19-C18-C17	120.9(5)
C20-C19-C18	120.8(4)	C19-C20-C21	121.1(4)
C20-C21-C16	116.9(4)	C20-C21-C22	120.8(4)
C16-C21-C22	122.3(4)	C21-C22-C24	110.7(4)
C21-C22-C23	113.9(4)	C24-C22-C23	109.8(4)
C26-C25-C17	110.9(3)	C26-C25-C27	109.8(4)
C17-C25-C27	113.5(4)	N4-C28-N3	104.3(3)
N4-C28-Si2''	130.4(7)	N3-C28-Si2''	125.1(7)
N4-C28-Si2	121.3(4)	N3-C28-Si2	134.1(3)
N4-C28-Si2'	145.6(5)	N3-C28-Si2'	109.3(4)
C30-C29-N3	107.3(4)	C29-C30-N4	107.9(4)
C36-C31-C32	123.0(5)	C36-C31-N4	120.8(4)
C32-C31-N4	116.0(5)	C40-C32-C33	122.9(5)
C40-C32-C31	121.7(5)	C33-C32-C31	115.4(6)
C34-C33-C32	121.3(5)	C33-C34-C35	121.0(6)
C34-C35-C36	121.3(7)	C31-C36-C35	117.8(5)
C31-C36-C37	123.2(5)	C35-C36-C37	119.0(6)
C36-C37-C39	111.0(5)	C36-C37-C38	109.5(5)
C39-C37-C38	113.6(6)	C32-C40-C41	114.3(5)
C32-C40-C42	113.0(6)	C41-C40-C42	107.3(5)
C44-C43-C48	124.7(5)	C44-C43-N3	117.5(4)
C48-C43-N3	117.5(4)	C45-C44-C43	116.3(5)
C45-C44-C52	119.1(5)	C43-C44-C52	124.4(5)
C44-C45-C46	120.8(5)	C47-C46-C45	121.0(6)
C46-C47-C48	121.0(5)	C43-C48-C47	116.1(5)
C43-C48-C49	123.6(4)	C47-C48-C49	120.1(5)
C48-C49-C50	112.7(4)	C48-C49-C51	109.5(4)
C50-C49-C51	109.6(4)	C44-C52-C54	113.8(4)
C44-C52-C53	110.1(5)	C54-C52-C53	109.1(4)

O1-C55-Fe1	179.5(4)	O2-C56-Fe1	177.6(3)
O3-C57-Fe1	178.0(4)	C59-C58-C63	123.0(8)
C59-C58-C64	130.8(14)	C63-C58-C64	106.2(13)
C58-C59-C60	120.5(7)	C61-C60-C59	118.5(7)
C60-C61-C62	120.0(7)	C63-C62-C61	122.9(8)
C62-C63-C58	115.0(8)	C66-C65-C70	121.5(14)
C66-C65-C71	118.5(15)	C70-C65-C71	119.9(14)
C65-C66-C67	119.1(15)	C68-C67-C66	121.1(15)
C67-C68-C69	119.9(17)	C70-C69-C68	121.3(16)
C65-C70-C69	117.0(12)	C70'-C65'-C66'	124.0(13)
C70'-C65'-C71'	118.6(12)	C66'-C65'-C71'	116.7(14)
C67'-C66'-C65'	117.2(15)	C68'-C67'-C66'	115.2(13)
C67'-C68'-C69'	131.1(14)	C70'-C69'-C68'	111.5(14)
C65'-C70'-C69'	120.6(13)		

Table 18. Torsion angles (°) for **78·(toluene)₂**.

C2-N1-C1-N2	0.4(4)	C16-N1-C1-N2	-170.1(3)
C2-N1-C1-Si1	-169.9(3)	C16-N1-C1-Si1	19.7(6)
C2-N1-C1-Si1'	-174.4(8)	C16-N1-C1-Si1'	15.1(9)
C3-N2-C1-N1	-0.6(4)	C4-N2-C1-N1	171.0(3)
C3-N2-C1-Si1	170.4(3)	C4-N2-C1-Si1	-18.0(5)
C3-N2-C1-Si1'	173.2(9)	C4-N2-C1-Si1'	-15.2(11)
C1-N1-C2-C3	-0.1(5)	C16-N1-C2-C3	170.7(4)
N1-C2-C3-N2	-0.3(5)	C1-N2-C3-C2	0.6(5)
C4-N2-C3-C2	-171.6(4)	C1-N2-C4-C9	-91.1(5)
C3-N2-C4-C9	79.7(5)	C1-N2-C4-C5	90.9(5)
C3-N2-C4-C5	-98.4(5)	C9-C4-C5-C6	0.3(7)
N2-C4-C5-C6	178.2(4)	C9-C4-C5-C13	-178.6(5)
N2-C4-C5-C13	-0.7(7)	C4-C5-C6-C7	-0.6(8)
C13-C5-C6-C7	178.3(5)	C5-C6-C7-C8	1.1(9)
C6-C7-C8-C9	-1.3(8)	C5-C4-C9-C8	-0.5(7)
N2-C4-C9-C8	-178.5(4)	C5-C4-C9-C10	179.5(4)
N2-C4-C9-C10	1.6(6)	C7-C8-C9-C4	1.0(7)
C7-C8-C9-C10	-179.0(5)	C4-C9-C10-C11	-120.4(6)
C8-C9-C10-C11	59.6(7)	C4-C9-C10-C12	115.7(6)
C8-C9-C10-C12	-64.3(6)	C4-C5-C13-C14	-137.9(5)
C6-C5-C13-C14	43.2(7)	C4-C5-C13-C15	97.9(6)
C6-C5-C13-C15	-81.0(7)	C1-N1-C16-C17	-102.9(4)
C2-N1-C16-C17	87.7(5)	C1-N1-C16-C21	80.0(5)
C2-N1-C16-C21	-89.3(5)	C21-C16-C17-C18	-4.5(6)
N1-C16-C17-C18	178.6(3)	C21-C16-C17-C25	171.2(4)
N1-C16-C17-C25	-5.7(5)	C16-C17-C18-C19	1.5(6)
C25-C17-C18-C19	-174.3(4)	C17-C18-C19-C20	1.0(7)
C18-C19-C20-C21	-0.8(7)	C19-C20-C21-C16	-2.0(6)
C19-C20-C21-C22	176.0(4)	C17-C16-C21-C20	4.8(6)
N1-C16-C21-C20	-178.3(3)	C17-C16-C21-C22	-173.2(4)
N1-C16-C21-C22	3.7(6)	C20-C21-C22-C24	-91.7(5)
C16-C21-C22-C24	86.3(5)	C20-C21-C22-C23	32.6(6)
C16-C21-C22-C23	-149.5(4)	C16-C17-C25-C26	-90.8(5)
C18-C17-C25-C26	84.7(5)	C16-C17-C25-C27	145.0(4)
C18-C17-C25-C27	-39.5(5)	C30-N4-C28-N3	-0.6(5)
C31-N4-C28-N3	173.2(4)	C30-N4-C28-Si2''	-175.1(9)
C31-N4-C28-Si2''	-1.3(11)	C30-N4-C28-Si2	174.4(3)

C31-N4-C28-Si2	-11.8(6)	C30-N4-C28-Si2'	-167.7(7)
C31-N4-C28-Si2'	6.1(10)	C29-N3-C28-N4	0.6(5)
C43-N3-C28-N4	-173.0(4)	C29-N3-C28-Si2''	175.4(8)
C43-N3-C28-Si2''	1.9(9)	C29-N3-C28-Si2	-173.5(4)
C43-N3-C28-Si2	12.9(7)	C29-N3-C28-Si2'	172.9(4)
C43-N3-C28-Si2'	-0.7(6)	C28-N3-C29-C30	-0.3(5)
C43-N3-C29-C30	173.7(4)	N3-C29-C30-N4	-0.1(5)
C28-N4-C30-C29	0.5(5)	C31-N4-C30-C29	-173.6(4)
C28-N4-C31-C36	97.3(6)	C30-N4-C31-C36	-89.6(6)
C28-N4-C31-C32	-88.7(6)	C30-N4-C31-C32	84.4(6)
C36-C31-C32-C40	177.5(5)	N4-C31-C32-C40	3.7(7)
C36-C31-C32-C33	-3.6(7)	N4-C31-C32-C33	-177.4(4)
C40-C32-C33-C34	-175.3(6)	C31-C32-C33-C34	5.8(8)
C32-C33-C34-C35	-5.6(10)	C33-C34-C35-C36	2.9(10)
C32-C31-C36-C35	1.1(8)	N4-C31-C36-C35	174.7(4)
C32-C31-C36-C37	-179.2(5)	N4-C31-C36-C37	-5.7(7)
C34-C35-C36-C31	-0.6(8)	C34-C35-C36-C37	179.7(6)
C31-C36-C37-C39	114.1(6)	C35-C36-C37-C39	-66.2(6)
C31-C36-C37-C38	-119.6(6)	C35-C36-C37-C38	60.0(7)
C33-C32-C40-C41	79.8(7)	C31-C32-C40-C41	-101.3(6)
C33-C32-C40-C42	-43.3(7)	C31-C32-C40-C42	135.5(5)
C29-N3-C43-C44	-87.4(5)	C28-N3-C43-C44	85.5(5)
C29-N3-C43-C48	86.6(5)	C28-N3-C43-C48	-100.5(5)
C48-C43-C44-C45	1.3(7)	N3-C43-C44-C45	174.8(4)
C48-C43-C44-C52	-175.0(4)	N3-C43-C44-C52	-1.4(7)
C43-C44-C45-C46	0.0(8)	C52-C44-C45-C46	176.4(5)
C44-C45-C46-C47	-0.8(10)	C45-C46-C47-C48	0.4(10)
C44-C43-C48-C47	-1.6(7)	N3-C43-C48-C47	-175.1(4)
C44-C43-C48-C49	173.3(4)	N3-C43-C48-C49	-0.2(6)
C46-C47-C48-C43	0.7(8)	C46-C47-C48-C49	-174.4(5)
C43-C48-C49-C50	139.9(4)	C47-C48-C49-C50	-45.4(6)
C43-C48-C49-C51	-97.9(5)	C47-C48-C49-C51	76.9(5)
C45-C44-C52-C54	42.6(7)	C43-C44-C52-C54	-141.3(5)
C45-C44-C52-C53	-80.3(6)	C43-C44-C52-C53	95.8(6)
C63-C58-C59-C60	0.2(11)	C64-C58-C59-C60	177.1(10)
C58-C59-C60-C61	2.6(10)	C59-C60-C61-C62	-3.9(10)
C60-C61-C62-C63	2.5(11)	C61-C62-C63-C58	0.2(11)
C59-C58-C63-C62	-1.6(11)	C64-C58-C63-C62	-179.1(8)

C70-C65-C66-C67 -3.(3)
 C65-C66-C67-C68 3.(3)
 C67-C68-C69-C70 2.(4)
 C71-C65-C70-C69 -177.2(15)
 C70'-C65'-C66'-C67' 0.(3)
 C65'-C66'-C67'-C68' 4.(3)
 C67'-C68'-C69'-C70' 7.(2)
 C71'-C65'-C70'-C69' 169.2(13)

C71-C65-C66-C67 176.7(15)
 C66-C67-C68-C69 -2.(4)
 C66-C65-C70-C69 3.(2)
 C68-C69-C70-C65 -2.(3)
 C71'-C65'-C66'-C67' -170.4(17)
 C66'-C67'-C68'-C69' -9.(3)
 C66'-C65'-C70'-C69' -1.(2)
 C68'-C69'-C70'-C65' -2.(2)

Table 19. Coordinates of the B3LYP/6-311G** optimized geometry of **83-Ph**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	14	0	1.387431	-1.387577	1.784233
2	1	0	1.338119	-2.022833	3.126399
3	14	0	0.172392	0.659671	1.304897
4	16	0	4.254755	4.155696	-0.659143
5	16	0	3.488574	-0.884066	1.444070
6	16	0	-6.240078	-0.153653	-1.489716
7	16	0	-0.795919	-0.216765	-0.633805
8	7	0	-0.112476	-3.765584	1.029072
9	7	0	1.376961	-3.383528	-0.488284
10	7	0	4.069296	1.622252	0.389586
11	7	0	2.126312	2.575502	0.083784
12	7	0	-3.525045	-0.339167	-1.145576
13	7	0	-4.406176	1.341430	-0.058989
14	6	0	0.914992	-2.936859	0.706130
15	6	0	-0.288957	-4.723989	0.045940
16	1	0	-1.073828	-5.456792	0.103585
17	6	0	0.645477	-4.485372	-0.903041
18	1	0	0.848118	-4.973107	-1.839768
19	6	0	3.475905	2.795942	-0.061749
20	6	0	3.083309	0.717950	0.781526
21	6	0	1.851336	1.282484	0.596557
22	6	0	-4.737302	0.283502	-0.881461
23	6	0	-2.464646	0.342845	-0.515116
24	6	0	-3.021962	1.382400	0.147019
25	1	0	-2.564749	2.111720	0.789576
26	6	0	2.471200	-2.849031	-1.271602
27	6	0	3.684524	-3.531725	-1.275408
28	6	0	2.270669	-1.713585	-2.048327
29	6	0	4.726428	-3.053197	-2.062561
30	1	0	3.813667	-4.411025	-0.655587
31	6	0	3.324081	-1.241097	-2.827994
32	1	0	1.312405	-1.209121	-2.039981
33	6	0	4.547226	-1.906998	-2.835476
34	1	0	5.679317	-3.568507	-2.063433
35	1	0	3.183690	-0.350154	-3.427962
36	1	0	5.362883	-1.532706	-3.442635
37	6	0	-0.944589	-3.663644	2.205056
38	6	0	-0.818419	-4.621411	3.208606
39	6	0	-1.872196	-2.629826	2.297377
40	6	0	-1.636097	-4.534382	4.331433
41	1	0	-0.081468	-5.410281	3.115684
42	6	0	-2.678589	-2.549153	3.430777
43	1	0	-1.959404	-1.909577	1.493210
44	6	0	-2.562448	-3.498279	4.443565
45	1	0	-1.543049	-5.270446	5.120967
46	1	0	-3.397826	-1.743750	3.514688
47	1	0	-3.193418	-3.431120	5.321947
48	6	0	-3.382232	-1.480101	-1.997034
49	6	0	-2.739615	-1.349087	-3.225619
50	6	0	-3.886361	-2.714783	-1.592717

51	6	0	-2.588278	-2.463504	-4.047566
52	1	0	-2.370481	-0.378809	-3.533253
53	6	0	-3.740438	-3.822875	-2.421626
54	1	0	-4.406983	-2.792087	-0.647045
55	6	0	-3.088810	-3.700528	-3.648495
56	1	0	-2.092545	-2.359252	-5.005887
57	1	0	-4.150032	-4.779114	-2.115718
58	1	0	-2.984903	-4.563205	-4.297186
59	6	0	-5.290305	2.332901	0.462851
60	6	0	-4.919134	3.676508	0.380961
61	6	0	-6.486570	1.972272	1.084528
62	6	0	-5.742650	4.657173	0.927176
63	1	0	-3.996347	3.950333	-0.116018
64	6	0	-7.306445	2.961264	1.618422
65	1	0	-6.770577	0.931202	1.135096
66	6	0	-6.939555	4.303817	1.544637
67	1	0	-5.449357	5.698520	0.859806
68	1	0	-8.236970	2.677870	2.096902
69	1	0	-7.583270	5.068693	1.963594
70	6	0	1.120977	3.545071	-0.234422
71	6	0	0.243299	3.310637	-1.290041
72	6	0	1.022280	4.712874	0.521214
73	6	0	-0.743536	4.249115	-1.586949
74	1	0	0.332551	2.399952	-1.867594
75	6	0	0.038940	5.647684	0.216463
76	1	0	1.721566	4.884518	1.328947
77	6	0	-0.845349	5.418647	-0.837574
78	1	0	-1.424773	4.067103	-2.410105
79	1	0	-0.033893	6.558057	0.800240
80	1	0	-1.606122	6.153081	-1.077478
81	6	0	5.482909	1.406180	0.470989
82	6	0	6.093892	1.328065	1.720524
83	6	0	6.234851	1.273596	-0.694384
84	6	0	7.465158	1.098528	1.803095
85	1	0	5.497137	1.450942	2.615770
86	6	0	7.605499	1.053548	-0.604886
87	1	0	5.745020	1.362235	-1.654895
88	6	0	8.221999	0.961909	0.642205
89	1	0	7.940961	1.037451	2.775033
90	1	0	8.194098	0.960276	-1.510413
91	1	0	9.290714	0.791968	0.708048

Table 20. Coordinates of the B3LYP/6-311G** optimized geometry of **84-Ph**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	14	0	-0.045221	-0.052694	0.817932
2	14	0	-1.144493	2.142873	1.010551
3	16	0	5.842521	-0.421259	-1.948281
4	16	0	1.931852	0.332962	1.882100
5	16	0	-3.293949	-1.391307	-3.995108
6	16	0	-2.710367	2.774088	-0.387234
7	7	0	-1.967816	1.165090	2.372985
8	7	0	-1.756044	-0.746683	3.397636
9	7	0	3.918692	0.152022	-0.083753
10	7	0	4.287912	-1.993502	-0.291492
11	7	0	-2.802691	0.734496	-2.327577
12	7	0	-4.320431	-0.642823	-1.552623
13	6	0	-1.220267	0.035979	2.420516
14	6	0	-2.987919	1.095817	3.301832
15	1	0	-3.699294	1.890020	3.450278
16	6	0	-2.856408	-0.090636	3.950462
17	1	0	-3.409675	-0.510535	4.772552
18	6	0	-1.305133	-2.050273	3.780910
19	6	0	0.059475	-2.302278	3.911719
20	6	0	0.482172	-3.575279	4.285862
21	1	0	1.542697	-3.772247	4.389762
22	6	0	-0.445218	-4.583220	4.539819
23	1	0	-0.109082	-5.569940	4.835463
24	6	0	-1.807093	-4.319194	4.410528
25	1	0	-2.534216	-5.100581	4.597311
26	6	0	-2.242463	-3.054838	4.025187
27	6	0	-0.573765	3.773519	1.752432
28	6	0	-1.484746	4.732532	2.230633
29	6	0	-1.038040	5.932897	2.774802
30	1	0	-1.754416	6.660877	3.139332
31	6	0	0.328713	6.200210	2.845424
32	1	0	0.676674	7.136519	3.267608
33	6	0	1.244298	5.265193	2.370697
34	1	0	2.307927	5.468298	2.419445
35	6	0	0.798537	4.060739	1.828749
36	6	0	4.696636	-0.759934	-0.773519
37	6	0	3.041760	-0.505726	0.800945
38	6	0	3.284684	-1.828989	0.661269
39	1	0	2.846620	-2.667830	1.170858
40	6	0	4.743410	-3.273722	-0.731783
41	6	0	6.103869	-3.580738	-0.739165
42	6	0	6.515628	-4.848668	-1.136717
43	1	0	7.573285	-5.085602	-1.146527
44	6	0	5.580651	-5.809569	-1.518845
45	1	0	5.909113	-6.795099	-1.828396
46	6	0	4.223878	-5.496650	-1.508279
47	1	0	3.490429	-6.233580	-1.814601
48	6	0	3.802043	-4.227188	-1.120987
49	6	0	4.010521	1.571554	-0.265313
50	6	0	4.940315	2.300181	0.470647

51	6	0	5.025267	3.678752	0.296049
52	1	0	5.753832	4.247832	0.862075
53	6	0	4.183615	4.322460	-0.609741
54	1	0	4.254146	5.395483	-0.747544
55	6	0	3.255208	3.585932	-1.343062
56	1	0	2.600472	4.080800	-2.050730
57	6	0	3.168606	2.206560	-1.173937
58	6	0	-3.473472	-0.438888	-2.633760
59	6	0	-3.232402	1.237170	-1.085255
60	6	0	-4.169129	0.377584	-0.621866
61	1	0	-4.766721	0.424309	0.270663
62	6	0	-5.207444	-1.748509	-1.369796
63	6	0	-6.195589	-2.025901	-2.313395
64	6	0	-7.071534	-3.083976	-2.093729
65	1	0	-7.837567	-3.302677	-2.828516
66	6	0	-6.968872	-3.858880	-0.939290
67	1	0	-7.654306	-4.682346	-0.775129
68	6	0	-5.978836	-3.576849	-0.001781
69	1	0	-5.885316	-4.183570	0.891654
70	6	0	-5.091669	-2.524930	-0.217504
71	6	0	-1.804697	1.325761	-3.172271
72	6	0	-2.098378	2.493427	-3.870598
73	6	0	-1.126086	3.068250	-4.685231
74	1	0	-1.351358	3.978008	-5.229485
75	6	0	0.125573	2.469345	-4.808060
76	1	0	0.878299	2.911673	-5.450621
77	6	0	0.408169	1.294273	-4.112299
78	1	0	1.376729	0.819187	-4.217203
79	6	0	-0.555995	0.719869	-3.288593
80	1	0	6.823311	-2.829102	-0.446504
81	1	0	2.750116	-3.967570	-1.137633
82	1	0	2.460140	1.621831	-1.747227
83	1	0	5.594501	1.784431	1.162504
84	1	0	0.777475	-1.512716	3.727638
85	1	0	-3.299500	-2.855890	3.895120
86	1	0	1.526663	3.342864	1.469405
87	1	0	-2.552887	4.548158	2.173592
88	1	0	-4.297689	-2.316114	0.489786
89	1	0	-6.264559	-1.422970	-3.208142
90	1	0	-0.354900	-0.196192	-2.748371
91	1	0	-3.080447	2.940835	-3.779255

Table 21. Coordinates of the B3LYP/6-311G** optimized geometry of **85a-Me**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	14	0	-0.861435	0.778311	0.323968
2	14	0	1.404025	1.163877	0.548358
3	16	0	-6.439893	-2.260126	0.650029
4	16	0	-1.700070	-0.273744	-1.453475
5	16	0	7.668400	-0.596674	-0.613908
6	16	0	2.135120	-0.633474	-0.492772
7	7	0	-1.838135	3.338312	1.334822
8	7	0	-1.872520	3.369103	-0.828879
9	7	0	-4.195392	-1.043023	-0.401159
10	7	0	-3.916321	-3.150535	0.085346
11	7	0	4.910743	-0.543636	-0.769651
12	7	0	5.681337	-0.994477	1.220317
13	6	0	-1.540323	2.584053	0.236221
14	6	0	-2.338883	4.569076	0.957332
15	1	0	-2.626106	5.317298	1.675299
16	6	0	-2.370671	4.584036	-0.396770
17	1	0	-2.699131	5.345528	-1.082469
18	6	0	-4.847742	-2.143259	0.108381
19	6	0	-2.872042	-1.371335	-0.722455
20	6	0	-2.714789	-2.684453	-0.418770
21	6	0	6.080507	-0.710709	-0.061468
22	6	0	3.808464	-0.721562	0.071051
23	6	0	4.299492	-1.007843	1.304088
24	1	0	3.778424	-1.221220	2.220422
25	6	0	6.605436	-1.245251	2.313637
26	1	0	7.243868	-2.098172	2.077959
27	1	0	7.243582	-0.374699	2.474141
28	1	0	6.027066	-1.451996	3.213681
29	6	0	4.855263	-0.230080	-2.188220
30	1	0	4.293500	-0.996412	-2.724734
31	1	0	4.379569	0.739673	-2.346481
32	1	0	5.881454	-0.199794	-2.549912
33	6	0	-1.645272	2.923753	2.723298
34	1	0	-1.736055	1.837645	2.775787
35	1	0	-0.655132	3.212978	3.078163
36	1	0	-2.410754	3.393306	3.341087
37	6	0	-1.649544	3.033930	-2.233543
38	1	0	-0.684415	2.535743	-2.330052
39	1	0	-2.426481	2.368281	-2.606700
40	1	0	-1.639961	3.958201	-2.809865
41	6	0	-4.819868	0.254073	-0.580753
42	1	0	-4.395811	0.987177	0.109838
43	1	0	-4.678127	0.598173	-1.606396
44	1	0	-5.881283	0.132762	-0.370407
45	6	0	-4.185225	-4.506159	0.536555
46	1	0	-4.996653	-4.943016	-0.047652
47	1	0	-3.278438	-5.097107	0.411907
48	1	0	-4.483725	-4.500378	1.586057
49	1	0	-1.845370	-3.310143	-0.517285

Table 22. Coordinates of the B3LYP/6-311G** optimized geometry of **85b-Me**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	14	0	-0.789509	0.051029	-0.267888
2	14	0	1.240906	-0.605695	-1.163549
3	16	0	-6.918749	-0.956565	1.224945
4	16	0	-2.357878	-0.130770	-1.832857
5	16	0	7.045167	-2.221312	0.988714
6	16	0	2.496178	0.803021	0.025327
7	7	0	-0.560637	2.321335	1.545514
8	7	0	-1.026878	3.043660	-0.440583
9	7	0	-4.666264	-0.302337	-0.232245
10	7	0	-5.102101	-2.438562	-0.183315
11	7	0	4.662012	-0.862483	0.674030
12	7	0	6.217506	-0.269351	-0.736144
13	6	0	-0.799089	1.902449	0.269746
14	6	0	-0.634275	3.697067	1.624958
15	1	0	-0.465550	4.229381	2.544692
16	6	0	-0.936426	4.148895	0.383428
17	1	0	-1.090077	5.149752	0.019294
18	6	0	-5.557687	-1.225609	0.267372
19	6	0	-3.667152	-0.946354	-0.973338
20	6	0	-3.954381	-2.271718	-0.938679
21	6	0	5.966269	-1.118561	0.312598
22	6	0	4.119162	0.128419	-0.150686
23	6	0	5.096465	0.491449	-1.019632
24	1	0	5.079857	1.225790	-1.805324
25	6	0	7.491262	-0.207961	-1.433452
26	1	0	8.288251	0.061678	-0.738601
27	1	0	7.729708	-1.180939	-1.866024
28	1	0	7.417402	0.540417	-2.222049
29	6	0	3.966333	-1.555794	1.744735
30	1	0	3.498965	-0.832644	2.414300
31	1	0	3.200166	-2.221452	1.340657
32	1	0	4.707453	-2.142988	2.283987
33	6	0	-0.224360	1.450398	2.670760
34	1	0	-0.686980	0.476205	2.506659
35	1	0	0.857041	1.325111	2.739306
36	1	0	-0.609475	1.893693	3.588645
37	6	0	-1.255727	3.115875	-1.881876
38	1	0	-0.583757	2.418334	-2.382395
39	1	0	-2.283190	2.851747	-2.128385
40	1	0	-1.039544	4.130496	-2.213508
41	6	0	-4.784832	1.128309	-0.021399
42	1	0	-3.977042	1.495375	0.616462
43	1	0	-4.756743	1.651120	-0.978660
44	1	0	-5.739895	1.303006	0.471515
45	6	0	-5.755442	-3.703727	0.110496
46	1	0	-6.778488	-3.695528	-0.268755
47	1	0	-5.189242	-4.503040	-0.366510
48	1	0	-5.791384	-3.866539	1.188828
49	1	0	-3.428717	-3.098275	-1.383085

Table 23. Sample and crystal data for **83•(toluene)_{2.5}**

Identification code	83•(toluene)_{2.5}	
Chemical formula	$\text{C}_{197}\text{H}_{252}\text{N}_{12}\text{S}_8\text{Si}_4$	
Formula weight	3156.94 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.180 x 0.350 x 0.400 mm	
Crystal system	monoclinic	
Space group	C2/c (No. 15)	
Unit cell dimensions	$a = 54.583(4) \text{ Å}$	$\alpha = 90^\circ$
	$b = 14.5630(12) \text{ Å}$	$\beta = 110.778(2)^\circ$
	$c = 25.285(2) \text{ Å}$	$\gamma = 90^\circ$
Volume	18791(3) Å ³	
Z	4	
Density (calculated)	1.116 g/cm ³	
Absorption coefficient	0.174 mm ⁻¹	
F(000)	6808	

Table 24. Data collection and structure refinement for **83•(toluene)_{2.5}**

Theta range for data collection	2.14 to 25.25°
Index ranges	-65<=h<=65, -17<=k<=16, -30<=l<=29
Reflections collected	119971
Independent reflections	16953 [R(int) = 0.1164]
Coverage of independent reflections	99.7%
Max. and min. transmission	0.7454 and 0.6277
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	16953 / 274 / 1065
Goodness-of-fit on F²	1.094
$\Delta/\sigma_{\max}$	0.001
Final R indices	10627 data; R1 = 0.0997, wR2 = I>2σ(I) 0.2247 all data R1 = 0.1544, wR2 = 0.2499
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0507P) ² +195.1683P] where P=(F _o ² +2F _c ²)/3
Largest diff. peak and hole	0.538 and -0.389 eÅ ⁻³
R.M.S. deviation from mean	0.082 eÅ ⁻³

Table 25. Bond lengths (Å) for **83•(toluene)_{2.5}**

Si1-H1	1.441(19)	Si1-C1	1.909(6)
Si1-S2	2.183(2)	Si1-Si2	2.349(2)
Si2-C30	1.941(6)	Si2-S4	2.263(2)
S1-C28	1.669(6)	S2-C29	1.768(6)
S3-C55	1.675(6)	S4-C56	1.752(6)
N1-C1	1.345(7)	N1-C2	1.374(7)
N1-C16	1.454(7)	N2-C1	1.340(7)
N2-C3	1.381(7)	N2-C4	1.462(7)
N3-C28	1.375(7)	N3-C29	1.388(7)
N3-C43	1.444(7)	N4-C28	1.368(7)
N4-C30	1.386(7)	N4-C31	1.443(7)
N5-C55	1.362(7)	N5-C56	1.407(7)
N5-C70	1.440(7)	N6-C55	1.367(7)
N6-C57	1.381(7)	N6-C58	1.447(7)
C2-C3	1.330(8)	C4-C9	1.398(9)
C4-C5	1.403(9)	C5-C6	1.382(9)
C5-C13	1.496(9)	C6-C7	1.402(10)
C7-C8	1.358(10)	C8-C9	1.409(8)
C9-C10	1.505(9)	C10-C11	1.509(9)
C10-C12	1.515(10)	C13-C15	1.521(9)
C13-C14	1.522(9)	C16-C17	1.384(8)
C16-C21	1.409(8)	C17-C18	1.393(8)
C17-C25	1.532(8)	C18-C19	1.365(9)
C19-C20	1.380(9)	C20-C21	1.381(8)
C21-C22	1.514(8)	C22-C23	1.512(9)
C22-C24	1.518(9)	C25-C27	1.508(8)
C25-C26	1.522(8)	C29-C30	1.364(7)
C31-C36	1.398(8)	C31-C32	1.404(9)
C32-C33	1.419(8)	C32-C40	1.490(9)
C33-C34	1.357(10)	C34-C35	1.369(9)
C35-C36	1.400(8)	C36-C37	1.528(9)
C37-C39	1.520(9)	C37-C38	1.539(9)
C40-C41	1.511(9)	C40-C42	1.532(9)
C43-C48	1.377(8)	C43-C44	1.395(9)
C44-C45	1.387(8)	C44-C52	1.501(9)
C45-C46	1.368(9)	C46-C47	1.366(10)
C47-C48	1.413(8)	C48-C49	1.513(9)

C49-C51	1.503(10)	C49-C50	1.532(9)
C52-C54	1.479(12)	C52-C53	1.531(10)
C56-C57	1.345(8)	C58-C63	1.390(8)
C58-C59	1.407(8)	C59-C60	1.401(8)
C59-C67	1.514(9)	C60-C61	1.367(9)
C61-C62	1.394(9)	C62-C63	1.401(8)
C63-C64	1.517(8)	C64-C65	1.515(9)
C64-C66	1.512(9)	C67-C68	1.525(9)
C67-C69	1.538(9)	C70-C71	1.364(8)
C70-C75	1.421(8)	C71-C72	1.406(8)
C71-C79	1.530(9)	C72-C73	1.385(9)
C73-C74	1.367(9)	C74-C75	1.392(8)
C75-C76	1.511(9)	C76-C77	1.511(10)
C76-C78	1.533(9)	C79-C80	1.533(10)
C79-C81	1.546(10)	C82-C83	1.368(9)
C82-C87	1.408(9)	C82-C88	1.481(10)
C83-C84	1.374(10)	C84-C85	1.360(11)
C85-C86	1.390(10)	C86-C87	1.356(10)
C89-C94	1.418(14)	C89-C90	1.410(16)
C89-C95	1.533(16)	C90-C91	1.433(16)
C91-C92	1.412(15)	C92-C93	1.383(15)
C93-C94	1.401(15)	C89'-C90'	1.41(2)
C89'-C94'	1.446(16)	C89'-C95'	1.51(2)
C90'-C91'	1.43(2)	C91'-C92'	1.41(2)
C92'-C93'	1.38(2)	C93'-C94'	1.42(2)
C96-C97	1.369(11)	C96-C97	1.369(11)
C96-C100	1.473(14)	C97-C98	1.405(14)
C98-C99	1.478(16)	C99-C98	1.478(16)

Table 26. Bond angles (°) for **83·(toluene)_{2.5}**

H1-Si1-C1	97(2)	H1-Si1-S2	108(2)
C1-Si1-S2	108.65(18)	H1-Si1-Si2	112(2)
C1-Si1-Si2	123.89(18)	S2-Si1-Si2	106.57(9)
C30-Si2-S4	98.50(18)	C30-Si2-Si1	77.33(17)
S4-Si2-Si1	93.40(8)	C29-S2-Si1	83.0(2)
C56-S4-Si2	102.0(2)	C1-N1-C2	109.9(5)
C1-N1-C16	124.7(4)	C2-N1-C16	124.8(5)
C1-N2-C3	109.3(5)	C1-N2-C4	125.7(5)
C3-N2-C4	124.2(5)	C28-N3-C29	109.3(4)
C28-N3-C43	124.3(4)	C29-N3-C43	126.4(5)
C28-N4-C30	112.7(4)	C28-N4-C31	124.4(4)
C30-N4-C31	122.5(4)	C55-N5-C56	110.3(5)
C55-N5-C70	123.1(5)	C56-N5-C70	126.2(5)
C55-N6-C57	109.8(5)	C55-N6-C58	123.2(5)
C57-N6-C58	127.0(5)	N2-C1-N1	106.2(5)
N2-C1-Si1	133.1(4)	N1-C1-Si1	120.6(4)
C3-C2-N1	106.9(5)	C2-C3-N2	107.6(5)
C9-C4-C5	124.6(6)	C9-C4-N2	118.0(5)
C5-C4-N2	117.3(5)	C6-C5-C4	116.2(6)
C6-C5-C13	120.5(6)	C4-C5-C13	123.4(5)
C5-C6-C7	121.1(6)	C8-C7-C6	121.0(6)
C7-C8-C9	121.1(6)	C4-C9-C8	116.0(6)
C4-C9-C10	122.8(5)	C8-C9-C10	121.2(6)
C9-C10-C11	112.9(6)	C9-C10-C12	109.3(5)
C11-C10-C12	112.6(6)	C5-C13-C15	110.7(6)
C5-C13-C14	112.3(5)	C15-C13-C14	110.4(6)
C17-C16-C21	123.6(5)	C17-C16-N1	119.3(5)
C21-C16-N1	117.1(5)	C18-C17-C16	117.0(5)
C18-C17-C25	120.8(5)	C16-C17-C25	122.1(5)
C19-C18-C17	121.0(6)	C18-C19-C20	120.5(6)
C19-C20-C21	121.7(6)	C20-C21-C16	116.1(6)
C20-C21-C22	120.8(5)	C16-C21-C22	123.0(5)
C23-C22-C21	109.6(5)	C23-C22-C24	110.2(6)
C21-C22-C24	114.0(5)	C27-C25-C26	110.3(5)
C27-C25-C17	110.2(5)	C26-C25-C17	113.1(5)
N4-C28-N3	104.3(5)	N4-C28-S1	129.2(4)
N3-C28-S1	126.5(4)	C30-C29-N3	109.3(5)

C30-C29-S2	127.9(5)	N3-C29-S2	122.7(4)
C29-C30-N4	104.4(5)	C29-C30-Si2	127.4(4)
N4-C30-Si2	127.4(4)	C36-C31-C32	124.4(5)
C36-C31-N4	118.3(5)	C32-C31-N4	117.1(5)
C31-C32-C33	115.3(6)	C31-C32-C40	122.5(5)
C33-C32-C40	122.1(6)	C34-C33-C32	121.2(6)
C33-C34-C35	121.7(6)	C34-C35-C36	121.0(6)
C31-C36-C35	116.3(6)	C31-C36-C37	121.7(5)
C35-C36-C37	122.0(6)	C39-C37-C36	113.0(5)
C39-C37-C38	111.1(6)	C36-C37-C38	110.8(5)
C32-C40-C41	111.2(5)	C32-C40-C42	113.8(5)
C41-C40-C42	110.2(6)	C48-C43-C44	124.2(5)
C48-C43-N3	117.8(6)	C44-C43-N3	117.9(5)
C43-C44-C45	116.7(6)	C43-C44-C52	122.6(6)
C45-C44-C52	120.7(6)	C46-C45-C44	121.1(6)
C47-C46-C45	121.0(6)	C46-C47-C48	120.8(6)
C43-C48-C47	116.2(6)	C43-C48-C49	122.6(5)
C47-C48-C49	121.3(6)	C51-C49-C48	111.9(6)
C51-C49-C50	110.2(7)	C48-C49-C50	112.5(6)
C54-C52-C44	111.2(7)	C54-C52-C53	110.6(7)
C44-C52-C53	113.4(6)	N5-C55-N6	105.4(5)
N5-C55-S3	127.4(4)	N6-C55-S3	127.1(4)
C57-C56-N5	105.9(5)	C57-C56-S4	135.0(5)
N5-C56-S4	119.0(4)	C56-C57-N6	108.5(5)
C63-C58-C59	123.4(5)	C63-C58-N6	118.5(5)
C59-C58-N6	118.1(5)	C60-C59-C58	116.5(6)
C60-C59-C67	120.0(6)	C58-C59-C67	123.6(5)
C61-C60-C59	122.2(6)	C60-C61-C62	119.6(6)
C63-C62-C61	121.3(6)	C58-C63-C62	117.1(6)
C58-C63-C64	122.1(5)	C62-C63-C64	120.7(5)
C65-C64-C63	110.8(5)	C65-C64-C66	109.6(6)
C63-C64-C66	114.4(5)	C59-C67-C68	111.6(5)
C59-C67-C69	110.0(5)	C68-C67-C69	111.2(6)
C71-C70-C75	122.7(5)	C71-C70-N5	119.9(5)
C75-C70-N5	117.4(5)	C70-C71-C72	118.6(6)
C70-C71-C79	122.4(5)	C72-C71-C79	119.0(6)
C73-C72-C71	119.9(6)	C74-C73-C72	120.5(6)
C73-C74-C75	121.8(6)	C74-C75-C70	116.5(6)

C74-C75-C76	120.5(6)	C70-C75-C76	123.0(5)
C75-C76-C77	111.3(5)	C75-C76-C78	111.8(6)
C77-C76-C78	111.8(6)	C80-C79-C71	111.1(6)
C80-C79-C81	111.2(6)	C71-C79-C81	111.8(6)
C83-C82-C87	118.3(7)	C83-C82-C88	121.6(7)
C87-C82-C88	120.1(7)	C82-C83-C84	120.6(7)
C85-C84-C83	121.5(7)	C84-C85-C86	118.3(7)
C87-C86-C85	121.0(7)	C86-C87-C82	120.2(7)
C94-C89-C90	125.1(18)	C94-C89-C95	111.8(18)
C90-C89-C95	123.0(18)	C89-C90-C91	112.9(17)
C92-C91-C90	126.(2)	C91-C92-C93	114.0(19)
C92-C93-C94	125.7(18)	C89-C94-C93	113.7(18)
C90'-C89'-C94'	120(3)	C90'-C89'-C95'	120(3)
C94'-C89'-C95'	117(3)	C91'-C90'-C89'	106(2)
C90'-C91'-C92'	124(3)	C93'-C92'-C91'	114(3)
C94'-C93'-C92'	125(3)	C93'-C94'-C89'	109(3)
C97-C96-C97	119.5(15)	C97-C96-C100	120.3(7)
C97-C96-C100	120.3(7)	C98-C97-C96	121.0(13)
C97-C98-C99	118(2)	C98-C99-C98	115(2)

Table 27. Sample and crystal data for **84•(toluene)₂**.

Identification code	84•(toluene)₂
Chemical formula	C ₉₅ H ₁₂₂ N ₆ S ₄ Si ₂
Formula weight	1532.40 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.120 x 0.220 x 0.340 mm
Crystal system	monoclinic
Space group	P2 ₁ /n (No. 14)
Unit cell dimensions	a = 17.7211(15) Å b = 27.855(2) Å c = 18.2418(16) Å
Volume	8993.6(13) Å ³
Z	4
Density (calculated)	1.132 g/cm ³
Absorption coefficient	0.179 mm ⁻¹
F(000)	3304

Table 28. Data collection and structure refinement for **84•(toluene)₂**.

Theta range for data collection	2.14 to 25.25°
Index ranges	-21≤h≤21, -33≤k≤33, -21≤l≤21
Reflections collected	253811
Independent reflections	16265 [R(int) = 0.0871]
Max. and min. transmission	0.7456 and 0.6302
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	16265 / 205 / 998
Goodness-of-fit on F²	1.068
$\Delta/\sigma_{\max}$	0.001
Final R indices	12920 data; I>2σ(I) R1 = 0.0669, wR2 = 0.1760 all data R1 = 0.0859, wR2 = 0.1883
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0857P)^2+13.8780P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.834 and -0.637 eÅ ⁻³
R.M.S. deviation from mean	0.066 eÅ ⁻³

Table 29. Bond lengths (Å) for **84•(toluene)₂**.

Si1-C1	1.952(3)	Si1-S2	2.2181(11)
Si1-Si2	2.4164(11)	Si2-N1	1.838(3)
Si2-C16	1.889(3)	Si2-S4	2.1502(11)
S1-C28	1.677(3)	S2-C29	1.743(3)
S3-C55	1.664(3)	S4-C56	1.747(3)
N1-C1	1.355(4)	N1-C2	1.389(4)
N2-C1	1.346(4)	N2-C3	1.384(4)
N2-C4	1.440(4)	N3-C28	1.364(4)
N3-C29	1.413(4)	N3-C43	1.437(4)
N4-C28	1.361(4)	N4-C30	1.383(4)
N4-C31	1.441(4)	N5-C55	1.368(4)
N5-C56	1.395(4)	N5-C70	1.442(4)
N6-C55	1.356(4)	N6-C57	1.392(4)
N6-C58	1.439(4)	C2-C3	1.348(5)
C4-C9	1.392(5)	C4-C5	1.399(5)
C5-C6	1.391(5)	C5-C13	1.518(5)
C6-C7	1.378(5)	C7-C8	1.374(5)
C8-C9	1.393(5)	C9-C10	1.515(5)
C10-C11	1.504(7)	C10-C12	1.520(6)
C13-C14	1.514(5)	C13-C15	1.521(6)
C16-C21	1.407(5)	C16-C17	1.409(5)
C17-C18	1.402(5)	C17-C25	1.514(5)
C18-C19	1.369(6)	C19-C20	1.371(6)
C20-C21	1.395(5)	C21-C22	1.519(5)
C22-C23	1.516(6)	C22-C24	1.526(5)
C25-C27	1.525(5)	C25-C26	1.529(5)
C29-C30	1.344(4)	C31-C32	1.399(5)
C31-C36	1.397(5)	C32-C33	1.389(5)
C32-C40	1.513(6)	C33-C34	1.365(6)
C34-C35	1.373(6)	C35-C36	1.396(5)
C36-C37	1.516(5)	C37-C38	1.515(6)
C37-C39	1.533(6)	C40-C41	1.523(6)
C40-C42	1.532(6)	C43-C48	1.391(4)
C43-C44	1.399(4)	C44-C45	1.396(5)
C44-C52	1.525(5)	C45-C46	1.377(5)
C46-C47	1.379(5)	C47-C48	1.397(4)
C48-C49	1.515(5)	C49-C50	1.528(5)

C49-C51	1.532(5)	C52-C53	1.520(5)
C52-C54	1.525(6)	C56-C57	1.348(4)
C58-C63	1.388(5)	C58-C59	1.387(4)
C59-C60	1.392(5)	C59-C67	1.502(14)
C59-C67'	1.536(12)	C60-C61	1.384(5)
C61-C62	1.361(5)	C62-C63	1.395(5)
C63-C64	1.517(5)	C64-C65	1.540(6)
C64-C66	1.529(7)	C67-C69	1.528(14)
C67-C68	1.535(12)	C67'-C69'	1.522(11)
C67'-C68'	1.535(13)	C70-C75	1.398(5)
C70-C71	1.387(5)	C71-C72	1.390(5)
C71-C79	1.520(5)	C72-C73	1.386(6)
C73-C74	1.368(6)	C74-C75	1.389(5)
C75-C76	1.516(14)	C75-C76'	1.537(15)
C76-C78	1.507(12)	C76-C77	1.521(15)
C76'-C78'	1.527(12)	C76'-C77'	1.535(13)
C79-C81	1.524(5)	C79-C80	1.516(6)
C82-C83	1.39	C82-C87	1.39
C82-C88	1.426(8)	C83-C84	1.39
C84-C85	1.39	C85-C86	1.39
C86-C87	1.39	C89-C90	1.39
C89-C94	1.39	C89-C95	1.436(10)
C90-C91	1.39	C91-C92	1.39
C92-C93	1.39	C93-C94	1.39

Table 30. Bond angles (°) for **84·(toluene)₂**.

C1-Si1-S2	100.20(9)	C1-Si1-Si2	67.84(9)
S2-Si1-Si2	99.66(4)	N1-Si2-C16	114.67(14)
N1-Si2-S4	108.31(9)	C16-Si2-S4	100.11(10)
N1-Si2-Si1	78.78(9)	C16-Si2-Si1	126.58(10)
S4-Si2-Si1	125.49(5)	C29-S2-Si1	98.24(11)
C56-S4-Si2	104.53(11)	C1-N1-C2	108.7(3)
C1-N1-Si2	100.11(19)	C2-N1-Si2	151.2(2)
C1-N2-C3	109.0(3)	C1-N2-C4	124.1(3)
C3-N2-C4	126.9(3)	C28-N3-C29	109.9(2)
C28-N3-C43	123.1(2)	C29-N3-C43	127.0(2)
C28-N4-C30	110.1(2)	C28-N4-C31	125.6(3)
C30-N4-C31	124.1(3)	C55-N5-C56	110.5(2)
C55-N5-C70	123.4(2)	C56-N5-C70	126.0(2)
C55-N6-C57	110.6(2)	C55-N6-C58	123.9(2)
C57-N6-C58	125.2(2)	N2-C1-N1	107.4(3)
N2-C1-Si1	139.9(2)	N1-C1-Si1	110.4(2)
C3-C2-N1	107.2(3)	C2-C3-N2	107.6(3)
C9-C4-C5	123.4(3)	C9-C4-N2	118.4(3)
C5-C4-N2	118.2(3)	C4-C5-C6	116.7(3)
C4-C5-C13	122.3(3)	C6-C5-C13	120.9(3)
C7-C6-C5	121.3(3)	C8-C7-C6	120.4(3)
C7-C8-C9	121.2(3)	C4-C9-C8	116.9(3)
C4-C9-C10	123.2(3)	C8-C9-C10	119.9(3)
C9-C10-C11	112.4(4)	C9-C10-C12	110.7(4)
C11-C10-C12	111.0(4)	C5-C13-C14	113.1(3)
C5-C13-C15	110.1(3)	C14-C13-C15	109.7(3)
C21-C16-C17	119.9(3)	C21-C16-Si2	118.3(2)
C17-C16-Si2	121.8(2)	C16-C17-C18	118.8(3)
C16-C17-C25	123.2(3)	C18-C17-C25	118.1(3)
C19-C18-C17	120.8(4)	C18-C19-C20	120.4(4)
C19-C20-C21	121.2(4)	C16-C21-C20	118.7(3)
C16-C21-C22	122.2(3)	C20-C21-C22	118.8(3)
C21-C22-C23	110.1(3)	C21-C22-C24	114.4(3)
C23-C22-C24	110.9(3)	C17-C25-C27	112.4(3)
C17-C25-C26	111.7(3)	C27-C25-C26	111.0(3)
N3-C28-N4	105.6(2)	N3-C28-S1	128.3(2)
N4-C28-S1	126.1(2)	C30-C29-N3	106.1(3)

C30-C29-S2	129.7(2)	N3-C29-S2	124.2(2)
C29-C30-N4	108.3(3)	C32-C31-C36	123.1(3)
C32-C31-N4	118.2(3)	C36-C31-N4	118.6(3)
C33-C32-C31	116.8(4)	C33-C32-C40	121.0(3)
C31-C32-C40	122.1(3)	C32-C33-C34	121.6(4)
C35-C34-C33	120.4(3)	C34-C35-C36	121.3(4)
C35-C36-C31	116.7(4)	C35-C36-C37	121.0(4)
C31-C36-C37	122.4(3)	C36-C37-C38	111.5(4)
C36-C37-C39	113.6(3)	C38-C37-C39	109.1(4)
C32-C40-C41	112.2(3)	C32-C40-C42	110.8(3)
C41-C40-C42	110.4(3)	C48-C43-C44	122.5(3)
C48-C43-N3	118.4(3)	C44-C43-N3	119.0(3)
C45-C44-C43	117.1(3)	C45-C44-C52	120.9(3)
C43-C44-C52	122.0(3)	C44-C45-C46	121.3(3)
C45-C46-C47	120.4(3)	C46-C47-C48	120.5(3)
C43-C48-C47	118.0(3)	C43-C48-C49	122.8(3)
C47-C48-C49	119.1(3)	C48-C49-C50	110.2(3)
C48-C49-C51	111.2(3)	C50-C49-C51	111.5(3)
C44-C52-C53	112.2(3)	C44-C52-C54	112.4(3)
C53-C52-C54	110.1(4)	N6-C55-N5	105.0(2)
N6-C55-S3	127.4(2)	N5-C55-S3	127.7(2)
C57-C56-N5	106.6(3)	C57-C56-S4	134.5(2)
N5-C56-S4	118.9(2)	C56-C57-N6	107.3(3)
C63-C58-C59	123.7(3)	C63-C58-N6	117.9(3)
C59-C58-N6	118.4(3)	C60-C59-C58	116.5(3)
C60-C59-C67	120.2(8)	C58-C59-C67	123.3(8)
C60-C59-C67'	123.9(8)	C58-C59-C67'	119.6(8)
C59-C60-C61	121.3(3)	C62-C61-C60	120.3(3)
C61-C62-C63	121.0(3)	C58-C63-C62	117.1(3)
C58-C63-C64	122.5(3)	C62-C63-C64	120.3(3)
C65-C64-C63	111.1(4)	C65-C64-C66	112.1(3)
C63-C64-C66	111.6(4)	C59-C67-C69	114.5(13)
C59-C67-C68	111.9(11)	C69-C67-C68	109.7(11)
C69'-C67'-C59	109.5(10)	C69'-C67'-C68'	110.1(10)
C59-C67'-C68'	110.9(13)	C75-C70-C71	124.6(3)
C75-C70-N5	116.9(3)	C71-C70-N5	118.5(3)
C70-C71-C72	116.5(3)	C70-C71-C79	121.8(3)
C72-C71-C79	121.7(3)	C73-C72-C71	120.6(4)

C74-C73-C72	121.0(3)	C73-C74-C75	121.2(4)
C70-C75-C74	116.1(3)	C70-C75-C76	120.3(9)
C74-C75-C76	123.4(9)	C70-C75-C76'	123.8(9)
C74-C75-C76'	120.0(9)	C78-C76-C75	109.4(13)
C78-C76-C77	111.2(13)	C75-C76-C77	106.4(14)
C78'-C76'-C75	118.0(18)	C78'-C76'-C77'	108.6(12)
C75-C76'-C77'	113.4(12)	C71-C79-C81	111.7(3)
C71-C79-C80	111.5(3)	C81-C79-C80	111.7(3)
C83-C82-C87	120.0	C83-C82-C88	115.8(7)
C87-C82-C88	124.2(7)	C84-C83-C82	120.0
C83-C84-C85	120.0	C86-C85-C84	120.0
C85-C86-C87	120.0	C86-C87-C82	120.0
C90-C89-C94	120.0	C90-C89-C95	105.1(9)
C94-C89-C95	134.9(9)	C89-C90-C91	120.0
C92-C91-C90	120.0	C91-C92-C93	120.0
C94-C93-C92	120.0	C93-C94-C89	120.0

Table 31. Coordinates of the B3LYP/6-311G** optimized geometry of **87-Me**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	2.442683	0.273251	-0.010674
2	5	0	-1.442053	-0.016639	-0.007940
3	35	0	4.192891	-0.515245	-0.007055
4	35	0	-1.834886	-1.213335	-1.613118
5	35	0	-1.818714	-0.923223	1.792698
6	35	0	-2.534205	1.699781	-0.147301
7	7	0	1.162639	-0.503284	-0.000372
8	7	0	2.108349	1.615066	-0.024540
9	6	0	0.135209	0.323441	-0.014482
10	6	0	0.657872	1.727460	-0.032018
11	1	0	0.268938	2.274820	0.835093
12	1	0	0.278336	2.247592	-0.919682
13	6	0	2.932841	2.811668	-0.036160
14	1	0	3.983600	2.526119	-0.031638
15	1	0	2.734892	3.409096	-0.930934
16	1	0	2.732419	3.427837	0.845218
17	6	0	1.070128	-1.971035	0.009370
18	1	0	0.248408	-2.280902	0.650316
19	1	0	0.887567	-2.328469	-1.004089
20	1	0	2.011467	-2.370079	0.380064

Table 32. Coordinates of the B3LYP/6-311G** optimized geometry of **88-Me**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	-2.935026	-0.382629	-0.043086
2	5	0	0.937885	0.004844	-0.011654
3	35	0	-4.709946	0.349665	-0.026256
4	7	0	-1.680426	0.431001	-0.006363
5	7	0	-2.562241	-1.712679	-0.092349
6	6	0	-0.622218	-0.364117	-0.038075
7	6	0	-1.110309	-1.783216	-0.098318
8	1	0	-0.710372	-2.347170	0.752883
9	1	0	-0.717208	-2.267767	-1.000159
10	6	0	-3.349953	-2.932816	-0.142166
11	1	0	-4.408813	-2.679190	-0.133846
12	1	0	-3.130844	-3.497631	-1.053057
13	1	0	-3.133764	-3.567979	0.721811
14	6	0	-1.649206	1.898151	0.046583
15	1	0	-0.863078	2.226946	0.722820
16	1	0	-1.450400	2.294337	-0.949637
17	1	0	-2.616838	2.247409	0.398982
18	53	0	1.380963	1.399046	-1.761993
19	53	0	1.318750	0.939367	2.049812
20	53	0	2.242814	-1.860952	-0.215824

Table 33. Sample and crystal data for **87**.

Identification code	87	
Chemical formula	$\text{C}_{26}\text{H}_{36}\text{B}_2\text{Br}_4\text{N}_2$	
Formula weight	717.82 g/mol	
Temperature	297(2) K	
Wavelength	0.71073 Å	
Crystal size	0.250 x 0.260 x 0.450 mm	
Crystal system	orthorhombic	
Space group	Pbca (No. 61)	
Unit cell dimensions	a = 19.6037(12) Å	$\alpha = 90^\circ$
	b = 17.1792(11) Å	$\beta = 90^\circ$
	c = 37.549(2) Å	$\gamma = 90^\circ$
Volume	12645.5(14) Å ³	
Z	16	
Density (calculated)	1.508 g/cm ³	
Absorption coefficient	5.108 mm ⁻¹	
F(000)	5696	

Table 34. Data collection and structure refinement for **87**.

Theta range for data collection	2.08 to 25.25°	
Index ranges	-22<=h<=23, -18<=k<=20, -45<=l<=45	
Reflections collected	107342	
Independent reflections	11448 [R(int) = 0.1521]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7454 and 0.1543	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	11448 / 4 / 625	
Goodness-of-fit on F²	1.010	
$\Delta/\sigma_{\max}$	0.001	
Final R indices	5934 data; I>2σ(I)	R1 = 0.0734, wR2 = 0.1574
	all data	R1 = 0.1618, wR2 = 0.1941
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0744P)^2+51.2858P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.955 and -1.494 eÅ ⁻³	
R.M.S. deviation from mean	0.102 eÅ ⁻³	

Table 35. Bond lengths (Å) for **87**.

B1-N2	1.359(10)	B1-N1	1.492(10)
B1-Br1	1.888(9)	B2-C1	1.579(11)
B2-Br4	1.963(10)	B2-Br2	2.006(10)
B2-Br3	2.063(10)	N1-C1	1.325(9)
N1-C15	1.466(9)	N2-C3	1.448(9)
N2-C2	1.445(9)	C1-C2	1.493(10)
C2-H2A	0.98(2)	C2-H2B	0.99(2)
C3-C8	1.385(11)	C3-C4	1.403(11)
C4-C5	1.392(12)	C4-C12	1.497(12)
C5-C6	1.364(13)	C6-C7	1.352(13)
C7-C8	1.388(11)	C8-C9	1.505(11)
C9-C11	1.501(12)	C9-C10	1.529(12)
C12-C14	1.501(16)	C12-C13	1.544(15)
C15-C20	1.391(12)	C15-C16	1.394(12)
C16-C17	1.385(12)	C16-C24	1.489(12)
C17-C18	1.372(14)	C18-C19	1.359(15)
C19-C20	1.396(12)	C20-C21	1.497(13)
C21-C23	1.530(15)	C21-C22	1.524(14)
C24-C26	1.498(15)	C24-C25	1.508(15)
B3-N4	1.343(10)	B3-N3	1.488(11)
B3-Br5	1.894(9)	B4-C27	1.600(12)
B4-Br6	1.987(11)	B4-Br8	1.995(11)
B4-Br7	2.058(14)	N3-C27	1.305(9)
N3-C41	1.464(9)	N4-C29	1.452(9)
N4-C28	1.462(9)	C27-C28	1.483(11)
C28-H28B	0.98(2)	C28-H28A	0.99(2)
C29-C30	1.373(11)	C29-C34	1.405(12)
C30-C31	1.381(12)	C30-C38	1.492(12)
C31-C32	1.367(15)	C32-C33	1.348(15)
C33-C34	1.385(12)	C34-C35	1.501(13)
C35-C36	1.515(14)	C35-C37	1.522(16)
C38-C40	1.524(14)	C38-C39	1.534(13)
C41-C46	1.378(12)	C41-C42	1.381(11)
C42-C43	1.395(12)	C42-C50	1.501(13)
C43-C44	1.360(15)	C44-C45	1.352(15)
C45-C46	1.385(13)	C46-C47	1.520(14)
C47-C49	1.538(16)	C47-C48	1.532(14)

C50-C51

1.535(14)

C50-C52

1.531(14)

Table 36. Bond angles (°) for **87**.

N2-B1-N1	106.9(7)	N2-B1-Br1	128.9(6)
N1-B1-Br1	124.1(6)	C1-B2-Br4	119.7(6)
C1-B2-Br2	108.7(6)	Br4-B2-Br2	110.4(5)
C1-B2-Br3	99.8(6)	Br4-B2-Br3	109.0(4)
Br2-B2-Br3	108.5(5)	C1-N1-C15	126.2(6)
C1-N1-B1	110.4(6)	C15-N1-B1	123.3(6)
B1-N2-C3	131.5(6)	B1-N2-C2	109.1(6)
C3-N2-C2	119.3(6)	N1-C1-C2	107.1(6)
N1-C1-B2	131.7(7)	C2-C1-B2	121.1(7)
H2A-C2-H2B	101(6)	H2A-C2-N2	113(4)
H2B-C2-N2	115(4)	H2A-C2-C1	111(4)
H2B-C2-C1	112(4)	N2-C2-C1	106.3(6)
C8-C3-C4	123.3(7)	C8-C3-N2	118.6(7)
C4-C3-N2	118.1(7)	C5-C4-C3	115.5(8)
C5-C4-C12	121.9(9)	C3-C4-C12	122.5(7)
C6-C5-C4	122.6(9)	C7-C6-C5	119.5(9)
C6-C7-C8	122.3(9)	C7-C8-C3	116.8(8)
C7-C8-C9	120.5(8)	C3-C8-C9	122.7(7)
C11-C9-C8	112.9(8)	C11-C9-C10	111.3(9)
C8-C9-C10	112.9(7)	C14-C12-C4	111.7(9)
C14-C12-C13	111.2(11)	C4-C12-C13	110.8(10)
C20-C15-C16	124.7(7)	C20-C15-N1	118.5(7)
C16-C15-N1	116.6(7)	C17-C16-C15	115.7(9)
C17-C16-C24	120.1(9)	C15-C16-C24	124.2(7)
C18-C17-C16	121.4(9)	C19-C18-C17	121.2(9)
C18-C19-C20	121.0(10)	C19-C20-C15	116.0(9)
C19-C20-C21	119.9(9)	C15-C20-C21	124.1(8)
C20-C21-C23	111.7(10)	C20-C21-C22	112.9(9)
C23-C21-C22	108.8(9)	C16-C24-C26	113.4(9)
C16-C24-C25	113.5(9)	C26-C24-C25	107.6(10)
N4-B3-N3	108.1(7)	N4-B3-Br5	128.8(7)
N3-B3-Br5	123.2(6)	C27-B4-Br6	117.8(7)
C27-B4-Br8	108.7(7)	Br6-B4-Br8	109.8(6)
C27-B4-Br7	100.7(7)	Br6-B4-Br7	110.8(6)
Br8-B4-Br7	108.5(5)	C27-N3-C41	126.8(6)
C27-N3-B3	109.6(6)	C41-N3-B3	123.3(6)
B3-N4-C29	132.0(6)	B3-N4-C28	108.3(6)

C29-N4-C28	119.4(6)	N3-C27-C28	108.4(6)
N3-C27-B4	132.2(7)	C28-C27-B4	119.3(7)
H28B-C28-H28A	104(6)	H28B-C28-N4	106(4)
H28A-C28-N4	114(4)	H28B-C28-C27	112(4)
H28A-C28-C27	116.(4)	N4-C28-C27	105.4(6)
C30-C29-C34	123.3(8)	C30-C29-N4	119.2(8)
C34-C29-N4	117.4(7)	C31-C30-C29	117.1(9)
C31-C30-C38	120.6(9)	C29-C30-C38	122.3(8)
C30-C31-C32	121.1(10)	C33-C32-C31	120.8(9)
C32-C33-C34	121.5(10)	C33-C34-C29	116.1(9)
C33-C34-C35	120.4(9)	C29-C34-C35	123.5(8)
C34-C35-C36	111.2(9)	C34-C35-C37	113.1(9)
C36-C35-C37	109.9(11)	C30-C38-C40	112.0(9)
C30-C38-C39	112.2(8)	C40-C38-C39	108.7(9)
C46-C41-C42	123.1(8)	C46-C41-N3	115.7(8)
C42-C41-N3	120.9(8)	C43-C42-C41	117.3(9)
C43-C42-C50	120.1(9)	C41-C42-C50	122.7(8)
C44-C43-C42	120.3(10)	C45-C44-C43	121.1(10)
C44-C45-C46	121.3(11)	C45-C46-C41	116.9(10)
C45-C46-C47	120.0(10)	C41-C46-C47	123.0(8)
C46-C47-C49	111.6(9)	C46-C47-C48	113.2(11)
C49-C47-C48	112.0(11)	C42-C50-C51	110.5(9)
C42-C50-C52	112.7(9)	C51-C50-C52	110.1(9)

Table 37. Sample and crystal data for **88**.

Identification code	88	
Chemical formula	$\text{C}_{26}\text{H}_{36}\text{B}_2\text{BrI}_3\text{N}_2$	
Formula weight	858.80 g/mol	
Temperature	297(2) K	
Wavelength	0.71073 Å	
Crystal size	0.150 x 0.210 x 0.400 mm	
Crystal system	orthorhombic	
Space group	$\text{P2}_1\text{2}_1\text{2}_1$ (No. 19)	
Unit cell dimensions	$a = 12.2369(6)$ Å	$\alpha = 90^\circ$
	$b = 14.6825(7)$ Å	$\beta = 90^\circ$
	$c = 18.0610(8)$ Å	$\gamma = 90^\circ$
Volume	$3245.0(3)$ Å ³	
Z	4	
Density (calculated)	1.758 g/cm ³	
Absorption coefficient	4.137 mm ⁻¹	
F(000)	1640	

Table 38. Data collection and structure refinement for **88**.

Theta range for data collection	2.01 to 27.88°
Index ranges	-16<= <i>h</i> <=16, -19<= <i>k</i> <=19, -23<= <i>l</i> <=23
Reflections collected	104369
Independent reflections	7743 [R(int) = 0.0503]
Max. and min. transmission	0.7457 and 0.2577
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7743 / 0 / 308
Goodness-of-fit on F²	1.072
$\Delta/\sigma_{\max}$	0.001
Final R indices	6716 data; I>2σ(I) R1 = 0.0378, wR2 = 0.0925 all data R1 = 0.0471, wR2 = 0.0982
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0485P)^2+3.1668P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.052(17)
Largest diff. peak and hole	0.851 and -1.603 eÅ ⁻³
R.M.S. deviation from mean	0.142 eÅ ⁻³

Table 39. Bond lengths (Å) for **88**.

B1-N2	1.342(8)	B1-N1	1.503(7)
B1-Br1	1.899(6)	B2-C1	1.615(9)
B2-I1	2.200(8)	B2-I2	2.229(8)
B2-I3	2.265(8)	N1-C1	1.311(8)
N1-C15	1.446(7)	N2-C3	1.443(7)
N2-C2	1.461(8)	C1-C2	1.491(8)
C3-C8	1.382(9)	C3-C4	1.406(10)
C4-C5	1.373(10)	C4-C12	1.536(11)
C5-C6	1.359(12)	C6-C7	1.369(12)
C7-C8	1.391(8)	C8-C9	1.513(10)
C9-C11	1.524(13)	C9-C10	1.493(13)
C12-C13	1.503(15)	C12-C14	1.526(14)
C15-C16	1.395(8)	C15-C20	1.404(8)
C16-C17	1.387(10)	C16-C24	1.512(11)
C17-C18	1.378(13)	C18-C19	1.358(12)
C19-C20	1.372(10)	C20-C21	1.519(10)
C21-C22	1.509(13)	C21-C23	1.532(13)
C24-C26	1.522(17)	C24-C25	1.56(2)

Table 40. Bond angles (°) for **88**.

N2-B1-N1	107.7(5)	N2-B1-Br1	128.7(4)
N1-B1-Br1	123.6(4)	C1-B2-I1	120.7(5)
C1-B2-I2	105.1(5)	I1-B2-I2	108.5(3)
C1-B2-I3	103.4(4)	I1-B2-I3	108.2(3)
I2-B2-I3	110.7(3)	C1-N1-C15	128.3(5)
C1-N1-B1	109.4(5)	C15-N1-B1	122.2(5)
B1-N2-C3	131.8(5)	B1-N2-C2	109.0(5)
C3-N2-C2	119.2(5)	N1-C1-C2	108.4(5)
N1-C1-B2	131.7(5)	C2-C1-B2	119.9(5)
N2-C2-C1	105.3(5)	C8-C3-C4	122.4(5)
C8-C3-N2	119.1(5)	C4-C3-N2	118.5(5)
C5-C4-C3	117.2(6)	C5-C4-C12	121.0(7)
C3-C4-C12	121.8(6)	C6-C5-C4	121.9(7)
C5-C6-C7	119.8(7)	C8-C7-C6	121.7(7)
C3-C8-C7	116.9(6)	C3-C8-C9	123.8(5)
C7-C8-C9	119.3(6)	C8-C9-C11	111.2(6)
C8-C9-C10	112.7(7)	C11-C9-C10	109.0(9)
C4-C12-C13	110.6(7)	C4-C12-C14	111.2(8)
C13-C12-C14	112.6(10)	C16-C15-C20	123.5(6)
C16-C15-N1	118.2(5)	C20-C15-N1	118.1(5)
C17-C16-C15	116.4(6)	C17-C16-C24	120.7(7)
C15-C16-C24	122.9(6)	C18-C17-C16	121.1(7)
C19-C18-C17	120.4(7)	C20-C19-C18	122.3(7)
C19-C20-C15	116.2(6)	C19-C20-C21	121.2(6)
C15-C20-C21	122.5(6)	C22-C21-C20	113.3(8)
C22-C21-C23	109.7(8)	C20-C21-C23	110.3(6)
C16-C24-C26	111.0(9)	C16-C24-C25	108.1(11)
C26-C24-C25	111.2(10)		

Table 41. Sample and crystal data for **89•toluene**.

Identification code	89•toluene	
Chemical formula	$\text{C}_{33}\text{H}_{45}\text{B}_2\text{Br}_5\text{N}_2$	
Formula weight	890.88 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.180 x 0.300 x 0.400 mm	
Crystal system	monoclinic	
Space group	$P2_1/c$ (No. 14)	
Unit cell dimensions	$a = 12.317(2)$ Å	$\alpha = 90^\circ$
	$b = 22.811(5)$ Å	$\beta = 109.718(6)^\circ$
	$c = 14.606(3)$ Å	$\gamma = 90^\circ$
Volume	$3863.3(13)$ Å ³	
Z	4	
Density (calculated)	1.532 g/cm ³	
Absorption coefficient	5.225 mm ⁻¹	
F(000)	1768	

Table 42. Data collection and structure refinement for **89•toluene**.

Theta range for data collection	2.08 to 26.02°
Index ranges	-15<=h<=15, -28<=k<=28, -18<=l<=18
Reflections collected	118311
Independent reflections	7600 [R(int) = 0.0999]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7454 and 0.2455
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7600 / 301 / 431
Goodness-of-fit on F²	1.033
$\Delta/\sigma_{\max}$	0.001
Final R indices	6114 data; I>2σ(I) R1 = 0.0521, wR2 = 0.1269 all data R1 = 0.0690, wR2 = 0.1352
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0584P)^2+18.8183P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	2.067 and -0.987 eÅ ⁻³
R.M.S. deviation from mean	0.123 eÅ ⁻³

Table 43. Bond lengths (Å) for **89•toluene**.

B1-N1	1.409(7)	B1-N2	1.467(7)
B1-Br1	1.885(6)	B2-Br5	2.003(6)
B2-Br3	2.003(6)	B2-Br4	2.019(6)
B2-Br2	2.026(6)	N1-C1	1.421(6)
N1-C15	1.444(6)	N2-C2	1.348(7)
N2-C3	1.458(6)	C1-H1A	0.98(2)
C1-H1B	0.99(2)	C1-C2	1.469(7)
C2-H2	0.96(2)	C3-C4	1.393(8)
C3-C8	1.398(8)	C4-C5	1.402(8)
C4-C12	1.506(8)	C5-C6	1.373(9)
C6-C7	1.394(9)	C7-C8	1.383(8)
C8-C9	1.523(8)	C9-C11	1.536(10)
C9-C10	1.524(8)	C12-C13	1.532(9)
C12-C14	1.540(8)	C15-C20	1.392(7)
C15-C16	1.406(8)	C16-C17	1.385(8)
C16-C24	1.531(9)	C17-C18	1.365(10)
C18-C19	1.383(9)	C19-C20	1.394(8)
C20-C21	1.513(8)	C21-C23	1.515(9)
C21-C22	1.544(9)	C24-C25	1.544(12)
C24-C26	1.527(10)	C27-C28	1.39
C27-C32	1.39	C27-C33	1.411(12)
C28-C29	1.39	C29-C30	1.39
C30-C31	1.39	C31-C32	1.39
C27'-C33'	1.477(12)	C27'-C28'	1.39
C27'-C32'	1.39	C28'-C29'	1.39
C29'-C30'	1.39	C30'-C31'	1.39
C31'-C32'	1.39		

Table 44. Bond angles (°) for **89-toluene**.

N1-B1-N2	106.4(4)	N1-B1-Br1	127.5(4)
N2-B1-Br1	126.1(4)	Br5-B2-Br3	110.9(3)
Br5-B2-Br4	110.0(3)	Br3-B2-Br4	109.4(3)
Br5-B2-Br2	107.9(3)	Br3-B2-Br2	109.5(3)
Br4-B2-Br2	109.1(3)	B1-N1-C1	109.6(4)
B1-N1-C15	129.4(4)	C1-N1-C15	121.0(4)
C2-N2-B1	108.8(4)	C2-N2-C3	123.2(4)
B1-N2-C3	128.0(4)	H1A-C1-H1B	85(6)
H1A-C1-N1	119(5)	H1B-C1-N1	118(5)
H1A-C1-C2	116(5)	H1B-C1-C2	113(5)
N1-C1-C2	105.6(4)	H2-C2-N2	119(4)
H2-C2-C1	132(4)	N2-C2-C1	109.5(4)
C4-C3-C8	124.4(5)	C4-C3-N2	117.7(5)
C8-C3-N2	117.9(5)	C3-C4-C5	116.6(5)
C3-C4-C12	123.6(5)	C5-C4-C12	119.8(5)
C6-C5-C4	120.6(6)	C5-C6-C7	121.0(5)
C8-C7-C6	121.0(6)	C7-C8-C3	116.5(5)
C7-C8-C9	120.7(5)	C3-C8-C9	122.8(5)
C8-C9-C11	111.0(5)	C8-C9-C10	113.4(5)
C11-C9-C10	109.4(6)	C4-C12-C13	111.3(5)
C4-C12-C14	110.3(5)	C13-C12-C14	110.0(5)
C20-C15-C16	123.0(5)	C20-C15-N1	118.4(4)
C16-C15-N1	118.6(5)	C17-C16-C15	117.1(6)
C17-C16-C24	120.4(5)	C15-C16-C24	122.4(5)
C18-C17-C16	121.4(6)	C17-C18-C19	120.5(5)
C18-C19-C20	121.2(6)	C15-C20-C19	116.8(5)
C15-C20-C21	123.2(5)	C19-C20-C21	120.0(5)
C20-C21-C23	112.0(5)	C20-C21-C22	110.1(5)
C23-C21-C22	110.8(5)	C16-C24-C25	109.8(6)
C16-C24-C26	111.1(7)	C25-C24-C26	111.1(6)
C28-C27-C32	120.0	C28-C27-C33	92.8(10)
C32-C27-C33	143.4(10)	C29-C28-C27	120.0
C28-C29-C30	120.0	C31-C30-C29	120.0
C32-C31-C30	120.0	C31-C32-C27	120.0
C33'-C27'-C28'	131.9(11)	C33'-C27'-C32'	105.6(10)
C28'-C27'-C32'	120.0	C27'-C28'-C29'	120.0
C30'-C29'-C28'	120.0	C29'-C30'-C31'	120.0

C32'-C31'-C30' 120.0

C31'-C32'-C27' 120.0

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