Amidinato silylene complexes for bond activation and catalysis

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2018

Khoo, S. Y. T. (2018). Amidinato silylene complexes for bond activation and catalysis.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/103657>

<https://doi.org/10.32657/10220/47433>

AMIDINATO SILYLENE COMPLEXES FOR BOND ACTIVATION AND CATALYSIS

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A thesis submitted to the Nanyang Technological University in partial
fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

ACKNOWLEDGMENTS

Firstly, I wish to offer my heartfelt thanks to my wonderful supervisor, Associate Professor Dr. Cheuk-Wai SO. If not for accepting me into his group and for his unchanging tolerance during my undergraduate honours year, as well as my entire PhD journey, this thesis would not be possible. His astute advice has allowed my research to bloom creatively; and I must admit, I have learnt a great deal from him—both in and out of the laboratory.

Secondly, I express my most generous appreciation to the delightful bunch called my colleagues—namely, Dr. CHAN Yuk Chi, Dr. LI Yan, Dr. Rahul KUMAR, Dr. Samuel HO, Dr. SHAN Yuliang, Dr. Celestine SEOW, Mr. Luthfi ISMAIL, Mr. CHIA Cher Chiek, Miss LEONG Bi Xiang, Miss CAO Jiajia and Mr. FAN Jun. Their cordial cooperation has shaped a conducive working environment and our ingenious—mostly whimsical—discussions have enlivened duller hours. Special mention goes to my undergraduate student—Miss Fiona NG.

Thirdly, technical assistance I received throughout my study cannot be neglected. I thank Dr. LI Yongxin and Dr. Rakesh GANGULY for solving all my X-Ray crystal structures; Miss GOH Ee Ling, Mr. Derek ONG and Mr. Keith LEUNG for their expertise in NMR. Particular thanks go to teaching lab staffs—Miss SEOW Ai Hua, Miss LIM Yen Lin, Miss Nicole TAN and Mr. Edmund CHOW—and Mr. WANG Wee Jian for sparing me supplies whenever needed.

Fourthly, my purely awesome batch mates—Miss SIM Ying, Mr. Sebastian QUEK and, again, Mr. Luthfi ISMAIL—deserve to be on this page for their ungodly patience in listening to all my rants and legitimate dedication in keeping me sane through these treacherous times. I am more than glad to say, “We have all survived.”

Additionally, I am indebted to the funds provided by the Nanyang President’s Graduate Scholarship (NPGS) and Chief Teaching Assistantship (CTA) for fully subsidizing my fees and overseas conferences.

Last, but certainly not least, I detail my gratitude towards my family for their unconditional support. Special mention goes to Mr. Mervyn CHUA for his absolute understanding and encouragement throughout this period.

Khoo Yee Teng, Sabrina (Aug 2018)

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List of Abbreviations and Symbols

Ar	2,6-diisopropylphenyl
br	broad
calcd.	calculated
cm ⁻¹	wavenumber
cod	1,5-cyclooctadiene
Cy	cyclohexyl
d	doublet
dec.	decomposed
DMAP	4-dimethylaminopyridine
EA	ethyl acetate
ESI	Electron Spray Ionization
<i>et al.</i>	and others
Et	ethyl
Et ₂ O	diethyl ether
g	gram(s)
GC	gas chromatography
h	hour(s)
HOMO	highest occupied molecular orbital
HRMS	High Resolution Mass Spectrometry
Hz/MHz	hertz/megahertz
<i>i</i> Pr	isopropyl
IR	Infrared
kcal	kilocalories
LUMO	lowest unoccupied molecular orbital
m	multiplet
M	molar (mol dm ⁻³)
M.p.	melting point
Me	methyl
MeLi	methyllithium
mL	millilitre(s)

μL	microlitre(s)
mmol/mol	millimole(s)/mole(s)
NMR	Nuclear Magnetic Resonance
Ph	phenyl
PhLi	phenyllithium
ppm	parts per million
q	quartet
s	singlet
sept	septet
t	triplet
<i>t</i>	<i>tert</i>
<i>t</i> Bu	<i>tert</i> -butyl
THF	tetrahydrofuran
TMS	trimethylsilyl (SiMe_3)
UV/Vis	Ultraviolet-Visible
WBI	Wiberg Bond Index
%	percentage
$\text{\AA}$	angstrom(s)
$^\circ$	degree(s)
$^\circ\text{C}$	degree(s) Celcius
α	alpha
β	beta
δ	chemical shift
ϵ	molar absorptivity
η	hapticity 'eta'
κ	bridging (bidentate) 'kappa'
λ_{max}	maximum wavelength
μ	bridging 'mu'
μB	Bohr magneton(s)
μ_{eff}	effective magnetic moment

List of Synthesized Compounds

Formula	Numbering	Page	Structure
$C_{54}H_{82}Cl_3Ir_3N_4Si_2$	1.21	31	
$C_{54}H_{82}Cl_3N_4Rh_3Si_2$	1.22	34	
$C_{46}H_{70}Cl_4N_4Rh_4Si_2$	1.33	34	
$C_{60}H_{92}Br_4Co_2N_8Si_4$	1.34	41	

Formula	Numbering	Page	Structure
$C_{38}H_{62}Br_4Fe_2N_4O_2Si_2$	2.10	98	
$C_{21}H_{44}BN_3Si_3/$ $C_{21}H_{41}BD_3N_3Si_3$	3.36/ 3.36-d₃	154	
$C_{17}H_{32}BN_3Si$	3.37	157	
$C_{22}H_{43}BF_3N_3O_3SSi_3/$ $C_{22}H_{41}BD_2F_3N_3O_3SSi_3$	3.39/ 3.39-d₂	160	
$C_{18}H_{31}BF_3N_3O_3SSi$	3.40	162	
$C_{16}H_{25}BClF_3N_2O_3SSi$	3.41	162	

Formula	Numbering	Page	Structure
$C_{39}H_{72}BF_3N_6O_3SSi_4$	3.42	164	
$C_{37}H_{66}BClF_3N_5O_3SSi_4$	3.43	164	
$C_{35}H_{60}BF_3N_6O_3SSi_2$	3.44	167	
$C_{29}H_{53}BF_3N_5O_3SSi_3$	3.45	168	
$C_{43}H_{82}BF_3N_6O_3SSi_6/$ $C_{42}H_{82}BDF_3N_6O_3SSi_6$	3.46/ 3.46-d	170	

Formula	Numbering	Page	Structure
$C_{30}H_{46}N_4Si$	3.49	174	
$C_{52}H_{87}BF_3N_7O_3SSi_4$	3.50	174	
$C_{49}H_{77}BF_3N_5O_3SSi_3$	3.52	174	
$C_{22}H_{42}F_3N_3O_3SSi_3$	3.53	178	
$C_{30}H_{49}N_3Si_2$	4.12	244	
$C_{30}H_{52}BN_3Si_2$	4.13	247	

Abstract

This thesis primarily describes the development of amidinato silylene complexes for the purposes of bond activation and catalysis.

In **Chapter 1**, the reactivity of amidinato silicon(I) dimer $[\text{LSi}]_2$ (**1.18**, $\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$) is explored with a series of group 9 transition metals. Amidinato silicon(I) dimer-metal complexes $[\text{LSi}\{\text{M}(\text{cod})-\mu\text{-Cl-M}(\text{cod})\}\text{SiL}][(\text{cod})\text{MCl}_2]$ (**1.21**: $\text{M} = \text{Ir}$; **1.22**: $\text{M} = \text{Rh}$) were afforded by coordination of Lewis base **1.18** to “(cod)MCl” and “(cod)M⁺” moieties. The Si–Si σ -bond can also undergo insertion in the case of Rh and Co to give dimeric rhodosilylene $[(\text{LSi})\mu\text{-}\{\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{cod})\}]_2$ (**1.33**) and dimeric cobaltosilylene $[(\text{LSi})\mu\text{-}\{\text{CoBr}(\text{LSiBr})\}]_2$ (**1.34**). “LSiCoBr” and “LSiBr” are postulated intermediates for the formation of the latter. A combination of catalytic amounts of **1.34**, phosphine, and Grignard reagent is capable of catalyzing the regioselective C–H functionalization of arylpyridines by alkynes. This stereoselectivity is governed by the steric effect between the substrates. **1.34** can also catalyze Kumada-type cross-coupling reactions between aryl chlorides and MesMgBr ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$).

An extension of this work is presented in **Chapter 2**, whereby $[\text{LSi}]_2$ (**2.9**) reacted with FeBr_2 without cleavage of the Si–Si σ -bond. Instead, a simple Lewis acid-base adduct $[\text{LSi}(\text{FeBr}_2 \cdot \text{thf})]_2$ (**2.10**) is yielded. **2.10** was found to be capable

of hydroboration of ketones and aldehydes with pinacolborane (HBpin) in the absence of any auxiliary reducing agents. Preliminary mechanistic studies indicate that carbonyls can be inserted into the Si–Fe bonds of **2.10**, and that the amidinato silicon(I) dimer **2.9** and $\text{FeBr}_2 \cdot \text{thf}_x$ function cooperatively, as Lewis base and acid respectively, to effect the catalysis via a zwitterionic intermediate.

Chapter 3 further explores silylenes as ligands, introducing a straightforward, stepwise, protocol to access a variety of silylene-supported boronium cations. In the presence of sterically-challenging Lewis bases, however, H_2 elimination and metal-free C–H borylation occurs affording endocyclic boronium salts. This formidable synthesis is postulated to proceed via a silylene borenium cation intermediate **3.46A**, which, in the can undergo the reverse reaction, H_2 addition, under ambient conditions to regenerate silylene borane precursor $[\text{L}\{(\text{SiMe}_3)_2\text{N}\}\text{Si} \rightarrow \text{BH}_3]$ (**3.36**) and $[\text{L}\{(\text{SiMe}_3)_2\text{N}\}\text{Si}(\text{H})]\text{OTf}$ (**3.53**) as identifiable products.

Lastly, **Chapter 4** documents our achievements in the challenging field of B–H bond activation. The amidinato amidosilylene $[L\{(\text{SiMe}_3)(\text{Ar})\text{N}\}\text{Si}:]$ (**4.12**) unit in $[L\{(\text{SiMe}_3)(\text{Ar})\text{N}\}\text{Si}:\rightarrow\text{BH}_2\text{OTf}]$ (**4.14**) was demonstrated to undergo intramolecular B–H bond activation to afford constitutional isomer $[\text{LB}(\text{H})\text{Si}(\text{H})(\text{OTf})\{\text{N}(\text{SiMe}_3)\text{Ar}\}]$ (**4.15**). **4.15** further reacts with DMAP to give $[(\mu-\kappa1:\kappa1\text{-L})\text{B}(\text{H})(\text{DMAP})\text{Si}(\text{H})\{\text{N}(\text{Ar})\text{SiMe}_3\}]\text{OTf}$ (**4.16**) via intermediate **4.15A**. While **4.16** can be obtained directly by refluxing **4.14** and DMAP, this reaction does not proceed through **4.15** or **4.15A**. Mechanistically, it is revealed that the formation of **4.15** and **4.16** both share the key intermediate **4.14A**. It undergoes triflate displacement in the presence of DMAP to give **4.16**; otherwise, it isomerizes to **4.15**. This pathway is validated by DFT calculations.

CHAPTER 1:

Amidinato Silylene Group 9 Metal Complexes and Their Applications in Catalysis[†]

1.1 Introduction

Great attention has been paid to silylenes of composition $[L_2Si:]$ (L = supporting ligand) in the past three decades.^[1] Their persistent limelight is largely attributed to their unique structures and reactivities, granted by the lone pair of electrons and vacant p orbital which exist simultaneously on the low valent silicon atoms (Chart 1.1). The immediate consequence is that these silicon atoms can act as donors and acceptors at the same time.

Chart 1.1 Schematic interpretation of silylene $[L_2Si:]$.

This unorthodox configuration appears not to fulfil the octet rule for the silicon atom as it bears only six valence electrons and a formal oxidation state of +2. Under such circumstances, it is only expected that these molecules have the tendency to oligomerize into polymeric substances containing Si–Si single bonds.

As stable, monomeric, silylenes are worthwhile synthetic targets for many fundamental reasons, significant efforts have been invested in their isolation. Despite the obvious challenges, several groups have successfully shown that

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kinetic and/or thermodynamic stabilization, via the use of sterically-hindered and/or electron-donating substituents respectively, is an especially handy strategy to achieve synthesis.^[2]

Chart 1.2 Examples of silylenes isolated over the years.

For instance, West utilized bulky *tert*-butyl substituents to isolate the first *N*-heterocyclic silylene (NHSi) **1.1** (Chart 1.2),^[2a] a heavier congener of the renowned *N*-heterocyclic carbene (NHC). Essentially pioneered by Roesky, smaller cyclic frameworks with a four-membered ring encasing the low valent silicon atom have also been extensively studied in the subsequent decade (**1.2** to **1.6**, Chart 1.2).^[2c,d] Although the σ -acceptor/ π -donor character of the amino substituents plays a vital role in the thermal stability of such compounds, scaling down the number of *N*-donor sites affords an outstanding, stable, cyclic (alkyl)(amino)silylene (cAASi) **1.7** (Chart 1.2), whose structure was characterized by Iwamoto in 2016.^[2h] Notably, purely alkyl ligands without classical donor atoms, too, have been substantiated as suitable stabilizers for silylenes. As early as 1999, a dialkylsilylene (**1.8**, Chart 1.2) stable at 0 °C was unveiled by Kira.^[2b] Lately, Power further expanded the ligand

scope by incorporating two bulky terphenyl thiolates on the low valent silicon center (**1.9**, Chart 1.2).^[2f] The sulfur atoms directly bound to the central metal are striking and in contrast to the traditionally-exploited period two elements. Another means of isolating strictly two-coordinate acyclic room temperature-stable silylenes unfolded independently from the collaboration of Aldridge and Jones. By combining Aldridge's strongly σ -donating boryl unit, which doubles as a reducing agent, and Jones' series of bulky amido ligand systems developed for the stabilization of low oxidation state, low coordinate s-, p- and d-block elements in a monodentate fashion, **1.10** (Chart 1.2) could be yielded.^[2e] Replacing the reductant with $(\text{thf})_2\text{K}[\text{Si}(\text{SiMe}_3)_3]$ furnishes a hypersilyl derivative, silylsilylene **1.11** (Chart 1.2), identified by the same programme a year later.^[2g]

Overall, the outcome is generally a “bottleable” silylene featuring incredible traits, namely concurrent donor- and acceptor-like behavior. Particularly, this ambiphilic property allows them to function as ancillary ligands in transition metal complexes, where there are synergy electron transfers between the low valent silicon atoms and transition metals.^[3] It has been discovered that the resulting transition metal-silylene complexes are catalytic intermediates,^[4] or bear the capacity to activate small molecules.^[5] The chemistry of such complexes has additionally been extended to the stabilization of otherwise highly reactive silylene species within the coordination sphere of transition metal fragments.^[6]

These compounds are known as metallosilylenes, typically bearing a M–Si(II) σ -bond. However, preparation of such metallo-substituted carbene analogues is a formidable challenge and can usually only be achieved by the metathesis reaction of heavier halocarbene analogues [REX] (E = Si, Ge, Sn; X = halide) and anionic transition metallate complexes. In 2011, Filippou and co-workers reported

that chromium-silylene complexes **1.12'** and **1.13'** were formed by heating halosilylene precursors **1.12** and **1.13** with $\text{Li}[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]$ in toluene (Scheme 1.1a).^[7] Earlier, in 2000, the group of Power described that treatment of arylchlorogermylene **1.14** with $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) gave the corresponding transition metallogermynes (**1.14-Cr/Mo/W**, Scheme 1.1b).^[8] Similarly, reaction of chlorostannylene dimers **1.15** and **1.16** with $\text{K}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ in diethyl ether afforded ferriostannylenes **1.15'** and **1.16'** respectively (Scheme 1.1c).^[9]

Scheme 1.1 Syntheses of metallo-substituted carbene analogues.

The syntheses of base-stabilized silicon(I) dimers, of composition $[\text{LSi}]_2$, have also been realized recently (**1.17** to **1.20**, Chart 1.3).^[10] The central silicon(I)

dimer core in **1.17** is stabilized by the NHC 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr),^[10a] while the same is effected by amidinate systems in **1.18** and **1.19**.^[10b,c] An amido-phosphine backbone can also be employed to access such silicon(I) dimers, as in **1.20**.^[10d]

Chart 1.3 Base-stabilized silicon(I) dimers.

Unlike their constitutional isomers, stable disilynes of composition [LSi≡SiL],^[11] a Si–Si single bond and a lone pair of electrons on each of these silicon atoms are characteristic of such compounds. Their reactivity revealed their powerful potential in the activation of small molecules, unsaturated substrates, etc.^[12] Likewise, they, together with other heavier group 14 element(I) dimers, have been demonstrated by our group to be versatile building blocks for the construction of complex molecules including: germatrisilacyclobutadiene, digermadistannacyclobutadiene and 2,4-diimino-1,3-disilacyclobutadiyl.^[13]

Owing to the presence of two low valent silicon centers, these dimers may exhibit different concerted effort between the heavier element(I) centers and transition metal centers. Hence, a difference in their coordination chemistry toward transition metals, in comparison to silylenes, should be anticipated, yet refreshing. Strangely, base-stabilized silicon(I) dimer-transition metal complexes in literature were unprecedented prior to 2015 (**1.21** and **1.22**, Chart 1.4).^[14] Published examples of heavier group 14 element(I) dimer-transition metal analogues has also

stagnated at one since its initial description of an unbroken Ge–Ge bond coordinated by $\text{Fe}(\text{CO})_4$ moieties by Roesky and co-workers in 2010 (**1.23**, Chart 1.4).^[15] The only other known reactivity was communicated by our group just last year, albeit with the cleavage of metal dimer.^[16] The seeming lack of exploration in this field sparked our interest in the coordination chemistry of base-stabilized silicon(II) dimers towards transition metals.

Chart 1.4 Known cases of base-stabilized heavier group 14 element(I) dimer-transition metal complexes as of 2017.

Furthermore, while increasing work is being performed to establish silylene-transition metal complexes as catalytically active species,^[4,5] the corresponding department for their base-stabilized silicon(II) dimer counterparts remains void. Advancements in the former is predominantly led by Driess, whose group illustrated that an iridium complex supported by a silylene pincer-type ligand (**1.24**, Chart 1.5) facilitates the C–H borylation of arenes with pinacolborane (HBpin) at a catalytic level.^[5c] When the metal center (Ir or Rh) is encompassed by a 1,5-cyclooctadiene (cod), chloride, and β -diketiminate-stabilized monochlorosilylene (**1.25** and **1.26**, Chart 1.5), catalytic amide reduction can be accomplished.^[5g] Going up the group, a novel cobalt complex ligated by a bis(silylene) with a ferrocenyl spacer (**1.27**, Chart 1.5) was also proven to mediate [2+2+2] cycloaddition reactions of acetonitrile and phenylacetylene at a 2.5 mol%

loading.^[5b] The akin iron(0) compounds (**1.28** and **1.29**, Chart 1.5) similarly transpired to be remarkable catalysts for the hydrogenation of ketones and aldehydes,^[5j] as did its electron-rich predecessors, a hydridosilylene-Fe(0) complex (**1.30**, Chart 1.5)^[5d] and pincer-type silylene-Fe(0) complex (**1.31**, Chart 1.5),^[5i] in the discipline of carbonyl hydrosilylation. Most recently, pincer-type silylene-Co(II) complex (**1.32**, Chart 1.5) catalyzed borylation of arenes regioselectively.^[5k]

Chart 1.5 Selected catalytically-active base-stabilized silylene-transition metal complexes.

Given the encouraging fact that the aforementioned endeavours have evidenced the proficiency of silylene-based transition metal complexes as catalysts in a wide range of organic transformations, we envision the possibility that the closely-related silicon(I)-transition metal complexes will display a comparable flair. In this context, we set out to probe the reactivity of amidinato silicon(I) dimer (**1.18**, Chart 1.3) towards a series of group 9 metal complexes, and the catalytic aptitude of selected obtained products. Our findings are detailed in the following section.

Given the diverse study of amidinato silicon(I) dimer **1.18** established by our group's and Roesky's (Scheme 1.2),^[17] we are interested to fill the gaps in terms of its reactivity towards transition metal complexes.

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(Scheme 1.3b).^[10c] It should be noted that this is in stark contrast to its analogues, which were afforded in yields averaging less than 10%. The most plausible reason for this quaint observation is apparent once one considers the respective reaction conditions, and is outlined in a recent review by the same author who described the favourable synthesis of **1.19**.^[18]

Scheme 1.3 Synthetic routes to base-stabilized silicon(I) dimers.

As seen in Scheme 1.3, reduction is imperative for the transformation of polyhalide precursors to the corresponding low valent species. However, as opposed to the long-established inorganic reducing agents, namely potassium graphite (KC₈) and elemental lithium used to obtain **1.17**, **1.18** and **1.20** (Scheme 1.3a), the hydrocarbon-soluble magnesium(I) dimer $[\{(\text{Mes})\text{Nacnac}\}\text{Mg}\}_2]$

(^{Mes}Nacnac = [(MesNCMe)₂CH]⁻; Mes = 2,4,6-Me₃C₆H₂) was employed to access silylene **1.19** (Scheme 1.3b). Evidently, the large disparity in yields is correlated with this change.

Although numerous landmark discoveries in the field of low valent main group species have been effected by engaging strongly-reducing substances, this extreme characteristic emerges as a shortcoming in the long-run.^[18] A common phenomenon accompanying the application of such harsh compounds is “over-reduction”, where the targeted low valent center is reduced further than desired or dissociates from its supporting ligands and deposits itself in an elemental form. Conceivably, products are lost in this process. In cases of intercalated reagents, such as metallic alloys or KC₈, the true composition is often unknown, giving rise to difficulties in controlling stoichiometry and selectivity; and, at times, even the reproducibility of reactions. Other problematic issues faced by conventional reducing agents include poor solubility in organic solvents. All of the above compound and compromise the yield as exemplified in Scheme 1.3a. Not to mention, these reducing agents are appreciable fire hazards due to their severe flammability upon exposure to air and moisture.

Accordingly, magnesium(I) dimers serve as safer alternatives to surmount these deficiencies. Their superiority is further illustrated by the remarkable preparation of the formal digermanium(0) species [IPr→Ge=Ge←IPr]^[19] as well as several other low valent complexes which tend to be elusive when reduction is conducted with KC₈ or alkali metals.^[20] Following this revelation, magnesium(I) dimers have been progressively implemented in the synthesis of inorganic/organometallic frameworks. However, they are not without their own drawbacks, such as tedious and lengthy preparation procedures. In order to

produce $[\{(\text{MesNacnac})\text{Mg}\}_2]$, the precursor $[(\text{MesNacnac})\text{MgI}]$, which is generated by treating the organic MesNacnac ligand with light-sensitive Grignard reagent $[\text{MeMgI}]$, has to be stirred for 5 days in the presence of a sodium mirror, posing significant dangers when handled on a large scale.^[21] On the other hand, the synthesis of traditional reducing agents is much simpler and less time-consuming.

Upon consulting all of the above, we sought to utilize a combination of protocols to optimize the synthesis of **1.18**. Instead of engaging the moderately-yielded trichlorosilane precursor, however, we synthesized the amidinate monochlorosilylene $[\text{L}(\text{Cl})\text{Si:}]$ via the channel developed by Roesky *et al.* in 2010.^[22] Obtained in an overall 81% yield from purchasable starting materials, $[\text{L}(\text{Cl})\text{Si:}]$ was reacted with KC_8 in an approximate 1:1.2 ratio at ambient temperature in toluene as reaction solvent (Scheme 1.4).

Scheme 1.4 Optimized synthetic route to amidinato silicon(I) dimer **1.18**.

After stirring the reaction mixture overnight, the expected **1.18** was crystallized from the filtrate and its structure was affirmed by ^1H NMR spectroscopy which corresponds well to the literature.^[10b] However, even to the best of our efforts, **1.18** could only be isolated in 45% yield. Nevertheless, this translates into a near fifteen-fold improvement from the original process. With this promising methodology in hand, we proceeded to test the reactivity of **1.18** obtained through this channel with a series of transition metal complexes.

1.2.2. Reactivity of Amidinato Silicon(I) Dimer (1.18) toward [Ir(cod)Cl]₂

Treatment of **1.18** with [Ir(cod)Cl]₂ in toluene at ambient temperature afforded the amidinato silicon(I) dimer-iridium complex [LSi{Ir(cod)-μ-Cl-Ir(cod)}SiL][(cod)IrCl₂] (**1.21**, Scheme 1.5) upon stirring overnight. In the positively-charged component, the Si(I) atoms act as two-electron donors to the Ir(I) atom and Ir(I) cation respectively, which are bridged by a Cl atom. The reaction appears to proceed through the coordination of “(cod)IrCl” moieties onto the Si(I) centers, followed by the displacement of the Cl⁻ anion, which may be due to steric hindrance, to give the [LSi{Ir(cod)-μ-Cl-Ir(cod)}SiL]⁺ cation. The Cl⁻ anion then reacts with another molecule of [Ir(cod)Cl]₂ to form [(cod)IrCl₂]⁻ anion. Varying from the reaction of the β-diketiminato chlorosilylene with [Ir(cod)Cl]₂ to furnish the silylene-iridium complex (**1.25**, Chart 1.5),^[5g] in which a standard coordination occurs and the iridium cation [(cod)Ir]⁺ and anion [(cod)IrCl₂]⁻ were not generated, our results are striking. Moreover, **1.21** represents one of the rare examples where the Si–Si σ-bond in the silicon(I) dimer is preserved. Only two such precedents have been noted with benzil^[17d] and cyclooctatetraene (COT)^[17f] by Roesky and co-workers (Scheme 1.2).

Scheme 1.5 Synthesis of iridium complex **1.21**.

The molecular structure of **1.21** is substantiated by single crystal X-ray diffraction (XRD) analysis and is depicted in Figure 1.1. Of the two independent

molecules present in the asymmetric unit, only one will be discussed for clarity. The Si1/2 atoms are shown to adopt a distorted tetrahedral geometry as they coordinate to the Ir1/2 atoms. A square planar environment is observed for the latter as they are bound by a bridging Cl, Si1/2 atom and the bidendate cod molecule. The Si1–Si2 bond (2.376(5) Å) is comparable to that of **1.18** (2.413(2) Å).^[10b] The Si1–Ir1 (2.334(4) Å) and Si2–Ir2 (2.307(4) Å) bonds are comparable to **1.25** (2.3164(8) Å).^[5g] They are also similar to other silyl iridium complexes (2.264(2) to 2.437(1) Å).^[23]

Figure 1.1 ORTEP drawing of **1.21** with thermal ellipsoids at the 30% probability level. As there are two independent molecules in the asymmetric unit with slightly different bond lengths and angles, only one independent molecule is discussed here for clarity. For the same reason, hydrogen atoms and solvent molecules are likewise elided. Selected bond lengths (Å) and bond angles (°): Ir1–Si1 2.334(4), Ir1–Cl1 2.373(3), Ir2–Si2 2.307(4), Ir2–Cl1 2.387(3), Si1–Si2 2.376(5), N1–Si1 1.838(11), N2–Si1 1.836(11), N3–Si2 1.832(11), N4–Si2 1.823(11), C5–N1 1.345(16), C5–N2 1.318(15), Ir5–Cl4 2.355(4), Ir5–Cl3 2.370(3); Si1–Ir1–Cl1 89.92(12), Si2–Ir2–Cl1 92.03(12), Ir1–Cl1–Ir2 123.76(15), Ir1–Si1–Si2 109.55(18), Ir2–Si2–Si1 105.62, N2–Si1–N1 71.1(5), N1–Si1–Ir1 115.1(4), N2–Si1–Si2 118.2(4), N4–Si2–N3 71.1(5), Cl4–Ir5–Cl3 89.50(13).

Highly air- and moisture sensitive red crystals of **1.21** were isolated in approximately 29% yield. They exhibit excellent solubilities in toluene and THF. Further characterization of **1.21** was completed by multinuclear NMR spectroscopy. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra display one set of resonances corresponding to the amidinate and cod ligands, which is in good agreement with the symmetric structure elucidated by XRD. The signal in $^{29}\text{Si}\{^1\text{H}\}$ NMR occurs at $\delta = 73.5$ ppm, which is slightly upfield shifted as compared to its precursor **1.18** ($\delta = 76.3$ ppm)^[10b] but significantly downfield shifted with respect to **1.25** ($\delta = 0.79$ ppm).^[5g]

1.2.3. Reactivity of Amidinato Silicon(I) Dimer (1.18) toward [Rh(cod)Cl]₂

Ensuing the result of **1.21**, we attempted the reaction of **1.18** with another group 9 metal(I) dimer complex [Rh(cod)Cl]₂ under identical conditions. Predictably, the lighter analogue, amidinato silicon(I) dimer-rhodium complex [LSi{Rh(cod)-μ-Cl-Rh(cod)}SiL][(cod)RhCl₂] (**1.22**, Scheme 1.6) was obtained, and is conceived to form via the same pathway as proposed above for **1.21**.

Scheme 1.6 Synthesis of rhodium complexes **1.22** and **1.33**.

Grown from a saturated toluene solution, good quality crystals of **1.22** were examined by single crystal XRD (Figure 1.2), corroborating that it is indeed isostructural to **1.21**. The Si–Si (2.388(2) Å) bond in **1.22** is comparable to that in **1.21** (2.376(5) Å); the Si–Rh bonds, measuring 2.2984(17) and 2.2951(17) Å, are comparable to that in the β-diketiminato chlorosilylene-rhodium complex (**1.26**, Chart 1.5).^[5g] Notably, these lengths present themselves shorter than typical Si–Rh single bonds (average: 2.32 Å)^[24] and that in cationic silylene-rhodium complex [(IPr→SiCl₂)₂Rh(CO)₂]⁺ (2.3605(8) Å),^[25a] suggesting some degree of π-back bonding from the rhodium to silicon atoms.

Figure 1.2 ORTEP drawing of **1.22** with thermal ellipsoids at the 10% probability level. Hydrogen atoms and solvent molecules are elided for clarity. Selected bond lengths (Å) and bond angles (°): Rh1-Si1 2.2984(17), Rh2-Si2 2.2951(17), Si1-Si2 2.388(2), Cl1-Rh1 2.3862(17), Cl1-Rh2 2.3871(17), Cl2-Rh3 2.3822(18), Cl3-Rh3 2.381(2); Si1-Rh1-Cl1 88.38(6), Si2-Rh2-Cl1 88.26(6), Rh1-Cl1-Rh2 126.34(7), Rh1-Si1-Si2 107.57(7), Rh2-Si2-Si1 108.04(7), N1-Si1-N2 71.3(2), N2-Si1-Rh1 118.04(16), N1-Si1-Si2 118.55(17), N3-Si2-N4 70.8(2), Cl3-Rh3-Cl2 92.00(7).

Yellow crystals of **1.22** were isolated in 76% yield. They are highly air- and moisture-sensitive but stable in solid state under an inert atmosphere. Analyses by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopies likewise revealed one set of signals for the amidinate and cod ligands. In $^{29}\text{Si}\{^1\text{H}\}$ NMR, a doublet arising from coupling to the adjacent rhodium atom was detected at $\delta = 76.8$ ppm (d, $^1J_{\text{Si-Rh}} = 76.6$ Hz), in a region similar to its precursor. This resonance falls within the range reported for other cationic silylene-rhodium adducts (Chart 1.6a)^[25] and is downfield shifted compared to those of neutral silylene-rhodium species (Chart 1.6b).^[5c,g]

Chart 1.6 Structures and $^{29}\text{Si}\{^1\text{H}\}$ NMR of (a) cationic; and (b) neutral silylene-rhodium complexes.

Amidst the considerable similarities between the aforementioned reactions, however, surfaced an aberration. Upon standing, dark red crystals were observed in the mother liquor of the reaction mixture between **1.18** and $[\text{Rh}(\text{cod})\text{Cl}]_2$. Single crystal XRD identified this substance as dimeric rhodosilylene $[(\text{LSi})\mu\text{-}\{\text{Rh}(\mu\text{-Cl})_2\text{Rh}(\text{cod})\}]_2$ (**1.33**, Scheme 1.6). It is postulated that **1.33** is formed via the insertion of $[\text{Rh}(\text{cod})\text{Cl}]_2$ into the Si-Si σ -bond, with concomitant displacement of two cod molecules. This reactivity distinguishes itself from that toward $[\text{Ir}(\text{cod})\text{Cl}]_2$, which does not provide the iridium analogue of **1.33** experimentally or feature two distinct binding motifs. Perhaps, this is attributable to the reduction potential of $[\text{Rh}(\text{cod})\text{Cl}]_2$ and $[\text{Ir}(\text{cod})\text{Cl}]_2$ by which the former enables one to cleave the Si-Si σ -bond in **1.18**.

The solid-state structure of **1.33** (Figure 1.3) unveils a planar and rhombic Si_2Rh_2 ring. Adopting distorted tetrahedral geometries, the Si1/1A atoms

coordinate with two nitrogen atoms of the amidinate ligands, as well as Rh2 and Rh2A. The latter are also bonded to two bridging Cl atoms to assume a distorted planar geometry (the dihedral angle of Si1–Si1A–Rh2–Cl2, 172.74°; Si1–Si1A–Rh2A–Cl1A, 175.12°). The Si1–Rh2A (2.2001(5) Å) and Si1–Rh2 (2.1792(5) Å) bonds are almost identical, which are shorter than that of **1.22**. The results are suggestive that there is significant π -back bonding from the Rh2/2A atoms to the Si1/1A atoms. While the Rh2–Rh2A bond length (2.9176(3) Å) indicates that it is a single bond, the Rh1···Rh2 separation of 3.0310(2) Å exceeds the sum of their covalent radii considerably, implying no interaction between Rh1 and Rh2. Additionally, the Si–N and C–N bonds of the amidinate ligands are comparable to those in **1.18** (Si–N, 1.866(4), 1.874(4); C–N, 1.331(6) Å).

Figure 1.3 ORTEP drawing of **1.33** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules are elided for clarity. Selected bond lengths (Å) and angles (°): Si1–Rh2 2.1792(5), Si1–Rh2A 2.2001(5), Rh2–Cl1 2.4346(4), Rh2–Cl2 2.4612(5), Rh1–Cl1 2.4015(5), Rh1–Cl2 2.4143(4), Si1–N1 1.8283(15), Si1–N2 1.8314(15), C9–N1 1.334(2), C9–N2 1.337(2); Si1–Rh2–Si1A 96.450(17), Rh2–Si1–Rh2A 83.552(17), Cl1–Rh2–Cl2 85.362(16), Si1–Rh2–Cl1 90.815(18), Si1A–Rh2–Cl2 88.065(17), N1–Si1–N2 71.19(7).

Characterization of **1.33** was also performed by multinuclear NMR spectroscopy. While the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are unexceptional, coinciding well with the amidinate and cod ligands, the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum exhibits a triplet at $\delta = 195$ ppm ($^1J_{\text{Si-Rh}} = 68.9$ Hz), with coupling to the two endocyclic Rh2/2A atoms. This signal is downfield shifted compared to **1.22** ($\delta = 76.8$ ppm) and is the most downfield signal amongst dinuclear transition metal bridged-silylene complexes ($\delta = 60$ to 160 ppm).^[26]

The intriguing structure of dimeric **1.33** stimulated our interest in its bonding situation, which was probed by density functional theory (DFT) calculations on the basis set of B3PW91/TZP-DKH. Meaningful frontier orbitals are highlighted in Figure 1.4 in which HOMO-30 depicts the lone pair electrons on the Si1/1A atoms donating to the Rh2/2A atoms; HOMO-10 displays the Rh2-Rh2A interaction; HOMO-7 and HOMO-8 demonstrate the Rh-Si σ orbitals; and HOMO-5 illustrates the π -back bonding from the Rh2/2A atoms to the Si1/1A atoms, justifying the shortened Si-Rh bonds.

Figure 1.4 Selected molecular orbitals of **1.33** (isovalue = 0.04).

Natural Population Analysis (NPA) charges of the Rh2/2A and Si1/1A atoms were found to be -0.85 e and +1.64 e respectively. The positively-charged silicon atoms concur with their abnormally deshielded signal observed in $^{29}\text{Si}\{^1\text{H}\}$ NMR. The steep gap between the NPA charges of Rh2/2A and Si1/1A denotes that the Si–Rh bonds are highly polarized. The Wiberg bond indices (WBI) of the Si–Rh bonds (0.728, 0.769) are slightly larger than that of the silyl rhodium(III) complex $[\text{H}_3\text{Si}-\text{RhH}_2]$ (Si–Rh, 2.256 Å; WBI, 0.7103; optimized by the B3PW91 method with 6-31+G** basis sets adopted on Si and H atoms and LanL08(f) basis set adopted on Rh atom), evidencing that the Si–Rh bonds in **1.33** are single bonds. WBI of the Rh2–Rh2A bond is calculated to be 0.229, hinting that there is an interaction

between the Rh2 and Rh2A atoms. These results collectively suggest that compound **1.33** is a dimer of two rhodosilylene complexes as illustrated in Scheme 1.7.

Scheme 1.7 Resonance interpretations of **1.33**.

1.2.4. Reactivity of Amidinato Silicon(I) Dimer (**1.18**) toward CoBr₂

Riding on the exciting syntheses of both charge-separated (**1.21** and **1.22**) and neutral (**1.33**) low valent silicon-transition metal complexes by simply switching the transition metal center, we were curious about the reactivity of **1.18** toward the lightest group 9 metal, cobalt. Regrettably, [Co(cod)Cl]₂, to the best of our knowledge, and unlike its heavier analogues, is not readily available on the market. Thus, we employed the use of commercially accessible CoBr₂ in our investigation.

Treatment of **1.18** with CoBr₂ in toluene at ambient temperature afforded the dimeric amidinato cobaltosilylene [(LSi) μ -{CoBr(LSiBr)}]₂ (**1.34**, Scheme 1.8) after 10 days. The protracted reaction time in comparison with those previously described is likely attributed to poor solubility of anhydrous CoBr₂ beads in the reaction solvent, which imaginably imparts the low yield (22%). No significant improvement is observed upon raising the reaction temperature.

Scheme 1.8 Synthesis of cobalt complex **1.34**.

The formation of **1.34** appears to proceed via the insertion of CoBr₂ into the Si–Si σ -bond (Scheme 1.9). This process generates “LSiBr” and “LSiCoBr” initially; dimerization of the latter follows and, finally, the coordination of “LSiBr” affords **1.34**. The solution magnetic moment of complex **1.34** was determined using the

Evans method ($\mu_{\text{eff}} = 2.80 \mu\text{B}$) and is lower than would be expected for two high spin Co(II) centers (spin only value expected for two uncoupled $S = 3/2$ Co(II) centers = $6.48 \mu\text{B}$), implying some degree of magnetic interaction or bonding between the two Co centers leading to an intermediate spin state.^[27] The paramagnetic character of **1.34** causes weak and broad ^1H NMR signals in the alkyl region at ambient temperature, conforming to four chemically-inequivalent sets of *tert*-butyl groups on the amidinate backbones. In addition, complex **1.34** was essentially silent in $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectroscopies.

Scheme 1.9 Proposed mechanism for the formation of **1.34**.

From the filtrate, black crystals of **1.34** were obtained and its molecular structure determined by single crystal XRD (Figure 1.5). The Si1–Co1 (2.220(1) Å) and Si1–Co1A (2.189(1) Å) are almost identical. They are comparable to the Si(II)–Co(II) donor-acceptor interactions displayed by bis(silylene)cobalt(II) bromide $[\{\text{L}(\text{Cl})\text{Si}\}]_2\text{CoBr}_2$ (2.1793(5), 2.1940(5) Å).^[28] Moreover, they are longer than the Si2–Co1 bonds (2.174(1) Å), which are formed by the donation of lone pair electrons on the Si2 atom to the vacant d orbital on the Co1 center.

Figure 1.5 ORTEP drawing of **1.34** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules are elided for clarity. Selected bond lengths (Å) and bond angles (°): Co1···Co1A 2.5240(6), Co1-Si1 2.220(1), Co1-Si1A 2.189(1), Co1-Br1 2.4452(7), Co1-Si2 2.174(1), Si2-Br2 2.295(1), Co1A-Si1A 2.220(1), Co1A-Si1 2.189(1), Co1A-Si2A 2.174(1), Co1A-Br1A 2.4452(7), Si2A-Br2A 2.295(1); Br1-Co1-Si1 115.25(3), Br1-Co1-Si1A 110.96(3), Br1-Co1-Si2 88.47(3), Br1-Co1-Co1A 133.27(2), Co1-Si1-N1 128.5(1), Co1-Si1-N2 134.4(1), Co1-Si1-Co1A 69.83(3), Co1A-Si1-N2 130.2(1), Br2-Si2-N3 98.5(1), Br2-Si2-N4 98.5(1), Br2-Si2-Co1 123.87(4), N4-Si2-Co1 127.0(1).

DFT studies were performed at B3LYP/6-31G(d) level of theory to gain further understanding of the electronic structure of **1.34**. The ground state of **1.34** is a triplet state as indicated by the negative value of ΔE_{st} (-27.4 kcal mol⁻¹, Table 1.1), being consistent with the solution magnetic moment. The WBI of the Co–Si bonds (0.55, 0.56, Figure 1.6) show that they are highly polarized. This result is in agreement with the contour plot of the Laplacian distribution $\nabla^2\rho(r)$ (Figure 1.7) which indicates that there is charge concentration in the middle of the Si–Co bonds, but more towards the Si atoms. Although the Co1–Co1A bond length (2.5240(6) Å) suggests that it is a single bond, neither charge concentration (Figure 1.7) nor electron density (Figure 1.8) was found between the cobalt atoms, confirming that there is no Co–Co interaction.

Table 1.1 $E(S_0)$, $E_u(T_1)$ and ΔE_{st} values^a for **1.34** at B3LYP/6-31G(d).

$E(S_0)/\text{a.u.}$	$E_u(T_1)/\text{a.u.}$	$\Delta E_{st}/\text{kcal mol}^{-1}$
-16988.9525375	-16988.9961918	-27.4

^a $\Delta E_{st} = E_u(T_1) - E(S_0)$; a positive value of ΔE_{st} indicates that singlet state is the ground state.

Figure 1.6 Bond lengths and Wiberg bond indices in the CoSiCoSi ring of **1.34** in its ground state.

Figure 1.7 Contour plot of the Laplacian distribution [$\nabla^2\rho(r)$] of the Co_2Si_2 ring in **1.34** in its ground state. Solid lines indicate charge concentration ($\nabla^2\rho(r) < 0$) while dotted lines mean charge depletion ($\nabla^2\rho(r) > 0$). Brown, blue, orange dots denote (3,-3), (3,-1), (3,+1) critical points, respectively. Solid lines connecting atomic nuclei (black) are the bond paths, and purple lines separating the atomic basins indicate the zero-flux surface crossing the molecular plane.

Figure 1.8 Color-filled map of ELF of the Co_2Si_2 ring of **1.34** in its ground state. ELF is within the range of [0,1]. A large ELF value means that higher degree of electrons localization. The results show that the electrons are more localized toward the Si atoms. In the middle of $\text{Co}\cdots\text{Co}$, the degree of electrons localization is slight.

Moreover, the spin density map of **1.34** (Figure 1.9) illustrates that the α electrons are populated on Co atoms and most of the β electrons are populated on Si atoms. The Mulliken spin population analysis of **1.34** (Table 1.2) illustrates that the total spin electron is 2.0, where there are about 3.4 α electrons populated on the d orbitals of the cobalt centres and 1.4 β electrons populated on the p orbitals of the Si atoms. On the basis of experimental data and theoretical studies, complex **1.34** should be considered as a dimer of two cobaltosilylene moieties as depicted in Scheme 1.10.

Figure 1.9 Spin density map of **1.34** in its ground state.

Table 1.2 Mulliken spin population analysis of **1.34** in its ground state at B3LYP/6-31G(d) level of theory.

Atom	Type	α pop.	β pop.	Total pop.	Spin pop.
Co	s	3.31908	3.25609	6.57517	0.06299
	p	6.63947	6.64458	13.28405	-0.00511
	d	4.54655	2.81960	7.36615	1.72695
	f	0.00114	0.00151	0.00265	-0.00037
Si	s	2.69002	2.76266	5.45268	-0.07263
	p	3.63498	4.22425	7.85923	-0.58928
	d	0.09434	0.10347	0.19781	-0.00914
Co	s	3.31104	3.24626	6.55730	0.06478
	p	6.63731	6.63515	13.27246	0.00216
	d	4.54059	2.82750	7.36809	1.71310
	f	0.00114	0.00151	0.00265	-0.00037
Si	s	2.68953	2.76234	5.45187	-0.07281
	p	3.63356	4.22436	7.85792	-0.59079
	d	0.09453	0.10377	0.19830	-0.00924
Total ^a	s	183.24453	183.26378	366.50831	-0.01925
	p	165.82122	167.21587	333.03709	-1.39464
	d	30.93196	27.51733	58.44929	3.41463
	f	0.00228	0.00302	0.00530	-0.00074

^a Sum of spin population of all atoms.

Scheme 1.10 Lewis structure of dimeric cobaltosilylene **1.34**.

1.2.5. Catalytic Studies of Amidinato Cobaltosilylene (1.34)

With a series of novel transition metal complexes in hand, and in accordance with the initial aim of our project, we were naturally keen to examine their catalytic potential. Recently, Driess *et al.* demonstrated that pincer-type NHSi-iridium complex **1.24** is proficient in catalyzing the C–H borylation of benzene (Scheme 1.11a),^[5c] a transformation, of C–H directly to C–B, that has only been established in the past two decades.^[29] Initially studied by stoichiometric reactions with transition metal-boryl complexes, it is now being accomplished catalytically by exploiting mostly rhodium- and iridium-based compounds. Classical ligands such as phosphines or cyclopentadienyl derivatives are frequently seen alongside the metals, but advancements in the use of carbene-based ligands have also been achieved.^[30] Amongst these results, it is the unconventional reactivity and selectivity effected by silylene-based catalyst **1.24** that is most incredible (Scheme 1.11a), proving that the stronger σ -donating NHSi is not simply a substitute for its isoelectronic analogues but, rather, a part of a new and emerging class of unique ligands.^[5c]

This exceptional quality was further evidenced when the same group reported selective catalytic reductive cleavage of amides by NHSi-Rh complex **1.26** (Scheme 1.11b),^[5g] which cannot be achieved well with regular salts such as $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ (COE = cyclooctene).^[31] In this arena, Milstein and Gade separately elucidated the possibility that silylene-rhodium complexes are key intermediates in hydrosilylation of olefins and ketones respectively.^[32] Besides, catalytic reduction of amides is of great importance in synthetic chemistry as it provides a pathway to access C–O and C–N cleavage products and should be worthwhile investigating.^[5c]

Scheme 1.11 Selected examples of reactions catalyzed by Ir/Rh/Co complexes.

Nonetheless, it has to be noted that noble metals have emerged increasingly unpopular in catalysis in light of several factors. Despite their superb performance, cost and toxicity are typically adequate to deter researchers and industries from utilizing these reagents. Consequently, inexpensive first-row

transition metals have risen as choice alternatives in recent years. One example is the successful replacement of Ru/Rh catalysts with Co in the field of alkyne hydroarylation established by Yoshikai in 2010 (Scheme 1.11c).^[33] Catalysis of other atom-economical reactions by cobalt include that of Kumada coupling between Grignards and alkyl, aryl, or vinyl halides,^[34] albeit only simple cobalt salts are engaged (Scheme 1.11d) in both this and the prior protocol. The only instances in which any silylene-complexed cobalt compounds have been employed as catalysts were that in [2+2+2] cycloaddition by **1.27** (Scheme 1.11e)^[5b] and that in regioselective arene borylation by **1.32** (Scheme 1.11f).^[5k] With these inspiring precedents, we decided to subject our dimeric cobaltosilylene (**1.34**) to the test in the unexplored departments of alkyne hydroarylation and Kumada cross-coupling.

Regarding the former, we attempted a model reaction between 2-phenylpyridine (**1.35a**) and diphenylacetylene (**1.36a**) as illustrated in Scheme 1.12. The progress of condition optimization is indexed in Table 1.3. Control experiments were conducted in the absence of catalyst (entry 1), ligand (entry 2) and Grignard reagent (entry 9), which resulted in no or trace products observed. Screening of ligands was performed at 5 mol% loading of **1.34** with a series of phosphines (entries 3 to 5) and amidinato amidosilylene [LSiNMe₂] (entry 6; L = PhC(N^tBu)₂). Aryl-substituted phosphines emerged superior, affording ca. 45% GC-yields and 45% isolated yield in the case of PPh₃ (entry 3). Conversely, increasing the amounts of alkyne (entries 7 and 8) or halving the amount of Grignard reagent (entry 10) only compromised the output of **1.37aa**. Much to our surprise, **1.37aa** was isolated exclusively as the (Z)-isomer (*E/Z* >> 1/99), as determined by ¹H and ¹³C NMR spectroscopies. This phenomenon is in sharp

contrast to Yoshikai's results, in which only the corresponding (*E*)-isomer was isolated using CoBr₂ as pre-catalyst.^[33]

Scheme 1.12 Hydroarylation of diphenylacetylene catalyzed by **1.34**.

Table 1.3 Condition optimization for hydroarylation of diphenylacetylene.

Entry	1.36a (equiv.)	Ligand	MeMgI (mol%)	Yield (%) ^a
1 ^b	1	—	200	n.d.
2	1	—	200	trace
3^c	1	PPh₃	200	45(45)
4	1	P(4-MeOC ₆ H ₄) ₃	200	46
5	1	PCy ₃	200	13
6 ^d	1	LSiNMe ₂	200	trace
7	1.5	PPh ₃	200	40
8	2	PPh ₃	200	38
9	1	PPh ₃	—	n.d.
10	1	PPh ₃	100	35

^a Determined by GC with *n*-dodecane as internal standard. ^b No catalyst was applied. ^c Isolated yield given in parentheses. ^d L = PhC(NtBu)₂.

Arylpyridines bearing electron-donating methyl and methoxy groups at the *para* position smoothly reacted with **1.36a** to give the corresponding (*Z*)-isomers of *ortho*-alkenylated products **1.37ba** and **1.37ca** (Chart 1.7). In contrast, the catalytic reaction of benzo[*h*]quinoline (**1.35d**) with **1.36a** only afforded the (*E*)-isomer **1.37da** (*E/Z* >99:1), whereby the stereoselectivity is considerably improved in comparison with that using the pre-catalyst CoBr₂ (*E/Z* = 84:16).^[33] When 4-octyne

(**1.36b**) was reacted with arylpyridines, the (*E*)-isomer of ortho-alkenylated products (**1.37ab** to **db**) were exclusively isolated.

Chart 1.7 Scope of arylpyridines and alkynes.^a

^a Reactions were performed under conditions stated in Table 1.2, entry 3; isolated yields are accounted; structures shown were obtained as the major product in a ratio of >99:1. ^b P(4-MeOC₆H₄)₃ was used instead of PPh₃.

The mechanism is not clear at present. On the basis of above results, it is proposed that the reaction proceeds through the reduction of **1.34** by the Grignard reagent, as well as coordination by the sterically hindered and labile phosphine ligand to form low-valent and -coordinate cobalt(I) active species (**1.34A**, Scheme 1.13). This hypothesis is evidenced by the fact that catalysis cannot proceed without the presence of PPh₃ (Table 1.3, entry 2). A phosphine-stabilized-like species was also identified in ³¹P NMR studies (δ 15.82 ppm, Figure 1.10) upon reacting **1.34** with two equivalents of PPh₃ (δ -4.42 ppm) in the presence of excess MeMgI in THF at 80 °C over a period of 1 hour. Similarly, DFT calculations elucidated that dissociation of **1.34** (ΔG = 0.0 kcal/mol; ΔH = 0.0 kcal/mol) to monomeric **1.34A''** (ΔG = 13.4 kcal/mol; ΔH = 34.1 kcal/mol) and phosphine-

donor-containing **1.34A'** ($\Delta G = 12.2$ kcal/mol; $\Delta H = 2.3$ kcal/mol) is thermodynamically favourable (Scheme 1.14).

Scheme 1.13 Proposed catalytic cycle for the hydroarylation of diphenylacetylene mediated by **1.34**.

Figure 1.10 Reaction of **1.34**, PPh_3 and MeMgI as monitored by ^{31}P NMR spectroscopy; xs. = excess.

Scheme 1.14 DFT-calculated dissociation of dimeric cobaltosilylene **1.34**; all energy values given in kcal/mol relative to **1.34** (B3LYP/6-31G(d)).

Subsequent oxidative addition of the *ortho*-C–H bond of arylpyridines to the cobalt centre, insertion of alkynes into the Co–H bond and reductive elimination affords the {(*E*)-alkenylaryl}-cobalt complex intermediate (**1.34D**, Scheme 1.13). The C=C bond then undergoes isomerization to form the anti-skeleton, resulting in the (*Z*)-isomer. In contrast, the rigid skeleton in benzo[*h*]quinoline (**1.35d**) may impede effective coordination of the C=C bond to the Co centre, and thereby the isomerization, which results in the formation of the (*E*)-isomer. A similar situation

was observed for 4-octyne (**1.36b**) due to the steric hindrance of the propyl substituents.

Following this interesting discovery, the versatile catalytic ability of **1.34** was further evaluated towards typical Kumada-type coupling reactions between aryl chlorides **1.38** and the Grignard reagent 2-mesitylmagnesium bromide **1.39** (Table 1.4). The results showed that **1.34** exhibits good catalytic activity (entries 1 to 5); electron-donating (Me, OMe) and -withdrawing (CF₃, F) groups were both tolerated. It should be noted that the use of 2-chlorotoluene **1.38f** led to lower yield of the corresponding product **1.40f** due to steric effect (entry 6).

Table 1.4 Kumada cross-coupling reactions of aryl chlorides and 2-mesitylmagnesium bromide.

Entry	R	Conversion (%) ^{a,b}	Yield (%) ^a
1	H	100	93
2	4-Me	92	91
3	4-OMe	100	>99
4	4-CF ₃	100	92
5	4-F	100	85
6	2-Me	59	47

^a Determined by GC with *n*-dodecane as internal standard. ^b Based on **1.38**.

1.3 Conclusion

The synthesis of amidinato silicon(I) dimer $[\text{LSi:}]_2$ (**1.18**, $\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$) was optimized by reduction of high-yield amidinato monochlorosilylene $[\text{L}(\text{Cl})\text{Si:}]$ with equimolar KC_8 . Its reactivity studies were then examined with transition metal complexes $[\text{M}(\text{cod})\text{Cl}]_2$ ($\text{M} = \text{Ir}, \text{Rh}$) and CoBr_2 . Reactions with $[\text{M}(\text{cod})\text{Cl}]_2$ afforded charge-separated silicon(I) dimer-iridium (**1.21**) and -rhodium (**1.22**) complexes, in which **1.18** acts as a Lewis base to coordinate with “(cod)MCl” and “(cod)M⁺” moieties. In the case of rhodium, the Si–Si σ -bond in **1.18** can also undergo insertion. DFT calculations, NMR spectroscopy and X-ray crystallography collectively suggest the product to be a dimeric rhosilylene (**1.33**). An akin structure (**1.34**) was accessed via the treatment of **1.18** with CoBr_2 after 10 days. Its formation is speculated to proceed through “LSiCoBr” and “LSiBr” intermediates. The paramagnetic nature of **1.34** was elucidated with the aid of Evans method and supported by DFT calculations.

In consideration of the growing interest to replace noble transition metal catalysts with their more abundantly-available, environmentally-friendly, and cost-effective counterparts, cobaltosilylene (**1.34**) was introduced into a series of organic transformations. A combination of **1.34**, phosphine and MeMgI is capable of regioselectively catalysing the addition of the *ortho*-C–H bond in arylpyridines with the $\text{C}\equiv\text{C}$ in alkynes. The stereoselectivity of the resulting *ortho*-alkenylated products relies on the steric effect between arylpyridines and alkynes. Moreover, **1.34** excels in catalysing Kumada-type coupling reactions between aryl chlorides and MesMgBr .

1.4 Experimental

1.4.1. Reactivity of 1.18

General considerations: All manipulations, unless otherwise stated, were carried out by using standard Schlenk and glovebox techniques under an atmosphere of high purity argon. Toluene and THF were dried and distilled over molten potassium. All NMR spectra were recorded on a JEOL ECA 400 spectrometer. ^1H NMR spectra were referenced to residual solvent peaks. All chemicals were used as received, unless stated otherwise. $[\text{L}(\text{Cl})\text{Si}]$ was synthesized according to literature procedure.^[22]

X-ray data collection and structural refinement: Intensity data for compounds **1.21**, **1.22**, **1.33** and **1.34** were collected by using a Bruker APEX II diffractometer. Reflections were measured at T / K (see section 1.5.1). The structures were solved by direct-phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2 .^[17] All nonhydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. A summary of selected crystallographic data is provided in section 1.5.1.

Synthesis of 1.18: Toluene (30 mL) was added to a mixture of $[\text{L}(\text{Cl})\text{Si}]$ (1.18 g, 4.01 mmol) and potassium graphite $[\text{KC}_8]$ (0.65 g, 4.80 mmol) at ambient temperature. The mixture was allowed to stir for 16 h. Upon filtration and concentration, dark red crystals of **1.18** were obtained.

Yield: 0.47 g (45%). ^1H NMR corresponded to literature.^[10b]

Synthesis of 1.21: Toluene (10 mL) was added to a mixture of **1.18** (0.103 g, 0.199 mmol) and $[\text{Ir}(\text{cod})\text{Cl}]_2$ (0.134 g, 0.199 mmol) at ambient temperature. The mixture was allowed to stir for 16 h. Upon filtration and concentration, red crystals of **1.21** were obtained.

Yield: 0.0866 g, (29%); M.p. 163 °C (dec).

^1H NMR (399.5 MHz, C_6D_6 , 24.7 °C): δ 1.59 (s, 36H, $t\text{Bu}$), 1.96-2.60 (br, 24H, CH_2), 3.48 (br, 4H, $=\text{CH}$), 4.28 (br, 4H, $=\text{CH}$), 5.37 (br, 4H, $=\text{CH}$), 6.96-7.13 (m, 8H, Ph), 8.67-8.69 (m, 2H, Ph) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, C_6D_6 , 24.7 °C): δ 31.62 (CMe_3), 32.11-32.82 (br, CH_2), 37.32 ($=\text{CH}$), 42.87 ($=\text{CH}$), 47.09 ($=\text{CH}$), 54.50 ($=\text{CH}$), 61.73 (CMe_3), 125.38, 129.98, 130.45, 131.99, 133.17 (Ph), 170.19 (NCN) ppm.

$^{29}\text{Si}\{^1\text{H}\}$ NMR (79.4 MHz, C_6D_6 , 24.4 °C): δ 73.53 ppm.

Elemental analysis calcd for $C_{54}H_{82}Cl_3Ir_3N_4Si_2$: C 42.50, H 5.41, N 3.67; found: C 42.30, H 5.19, N 3.63.

Synthesis of 1.22 and 1.33: Toluene (10 mL) was added to a mixture of **1.18** (0.103 g, 0.199 mmol) and $[Rh(cod)Cl]_2$ (0.0986 g, 0.200 mmol) at ambient temperature. The mixture was allowed to stir for 16 h. Upon filtration and concentration, yellow crystals of **1.22** were obtained. The mother liquor was filtered and further concentrated to afford dark red crystals of **1.33**.

1.22: Yield: 0.095 g, (76%); M.p. 135 °C (dec).

1H NMR (399.5 MHz, C_6D_6 , 24.7 °C): δ 1.63 (s, 18H, *t*Bu), 1.70 (s, 18H, *t*Bu), 2.05-2.34 (br, 24H, CH_2), 3.64 (br d, $^2J_{H-Rh} = 105.7$ Hz, 4H, =CH), 4.32 (br, 4H, =CH), 5.88 (br d, $^2J_{H-Rh} = 41.6$ Hz, 4H, =CH), 6.93-7.05 (m, 8H, Ph), 8.83-8.85 (m, 2H, Ph) ppm.

$^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6 , 24.6 °C): δ 30.62 (CMe_3), 31.90 (CMe_3), 33.23 (br, CH_2), 54.14 (br, CMe_3), 76.81 (d, $J_{C-Rh} = 13.4$ Hz, =CH), 78.30 (d, $J_{C-Rh} = 14.4$ Hz, =CH), 125.38, 129.94, 132.21, 133.19, 137.58 (Ph), 168.84 (NCN) ppm.

$^{29}Si\{^1H\}$ NMR (78.7 MHz, C_6D_6 , 25.2 °C): δ 76.82 (d, $^1J_{Si-Rh} = 76.6$ Hz) ppm.

Elemental analysis calcd for $C_{54}H_{82}Cl_3Rh_3N_4Si_2$: C 51.55, H 6.57, N 4.45; found: C 51.45, H 6.48, N 4.34.

1.33: Yield: 0.024 g, (19%); M.p. 195 °C.

1H NMR (395.9 MHz, C_6D_6 , 24.5 °C): δ 1.50 (s, 36H, *t*Bu), 1.56-1.60 (m, 8H, CH_2), 2.29-2.32 (m, 8H, CH_2), 4.67 (br s, 8H, =CH), 6.81-6.94 (m, 6H, Ph), 7.27-7.31 (m, 4H, Ph) ppm.

^{13}C NMR (99.55 MHz, C_6D_6 , 24.8 °C): δ 30.92 (CMe_3), 31.26 (CH_2), 32.22 (CH_2), 54.46 (CMe_3), 77.13 (d, $J_{C-Rh} = 13.4$ Hz, =CH), 78.55 (d, $J_{C-Rh} = 14.3$ Hz, =CH), 125.70, 128.85, 130.13, 131.65 (Ph), 172.75 (NCN) ppm.

$^{29}Si\{^1H\}$ NMR (79.52 MHz, C_6D_6 , 25.0 °C): δ 195.1 (t, $^1J_{Si-Rh} = 68.9$ Hz) ppm.

Elemental analysis calcd for $C_{46}H_{70}Cl_4N_4Rh_4Si_2$: C 42.88, H 5.48, N 4.35; found: C 42.61, H 5.33, N 4.01.

UV/vis (DME): $\lambda_{max}(\epsilon) = 410$ (2922), 634 (472 mol $^{-1}$ dm 3 cm $^{-1}$) nm.

Synthesis of 1.34: Toluene (30 mL) was added to a mixture of **1.18** (0.2858 g, 0.551 mmol, 1.0 equiv.) and CoBr_2 (0.1205 g, 0.551 mmol, 1.0 equiv.) at ambient temperature. The mixture was allowed to stir for 10 days. Upon filtration and concentration, black crystals of **1.34** were obtained.

Yield: 0.20 g, (22%); M.p. 165 °C (dec).

^1H NMR (395.9 MHz, C_6D_6 , 24.0 °C): δ 1.47 (s, 18H, *t*Bu), 1.73 (s, 18H, *t*Bu), 1.88 (s, 18H, *t*Bu), 2.04 (s, 18H, *t*Bu), 6.85-7.13 (m, 20H, Ph) ppm.

Elemental analysis calcd for [**1.34**· $2\text{C}_7\text{H}_8$] $\text{C}_{74}\text{H}_{108}\text{Br}_4\text{Co}_2\text{N}_8\text{Si}_4$: C 53.56, H 6.56, N 6.75; found: C 50.65, H 7.13, N 5.85.

$\mu_{\text{eff}} = 2.80 \mu\text{B}$ (Evans method, see section 1.5.2 for NMR spectrum).

1.4.2. Catalytic Studies

General considerations: All glassware were dried at 120 °C prior to use; an argon-filled glovebox was used when required. Toluene was dried using a MBraun Solvent purification system; THF was dried over molten potassium; dioxane was dried over CaH₂; anhydrous acetonitrile was purchased from Kanto and used directly. All NMR spectra were acquired on Bruker 500 MHz, 400 MHz or 300 MHz NMR spectrometers. ¹H NMR chemical shifts were recorded relative to TMS (δ 0.00) or residual solvent peaks. All chemicals were used as received, unless stated otherwise. GC internal standard, *n*-dodecane, was degassed with argon and dried over activated 4 Å molecular sieve beads before use. Flash chromatography was performed using Merck 40-63D 60 Å silica gel. GC analysis was performed on a Shimadzu GC-2010 instrument with Agilent J & W GC column DB-5MS-UI. GC/MS analysis was conducted on a Thermo Scientific DSQ II single quadrupole GC/MS instrument with Agilent J & W GC column DB-5MS-UI. Proof of purity of new compounds was demonstrated with copies of ¹H and ¹³C NMR spectra (see section 1.5.3).

Typical procedure for condition optimization for catalytic hydroarylation of diphenylacetylene with 2-phenylpyridine: In the glovebox, a Schlenk tube containing a magnetic stir bar was charged with **1.34** (5 mol%, 7.4 mg), ligand (20 mol%), 2-phenylpyridine (0.1 mmol, 14 μ L) and THF (1 mL). To the mixture was added a THF solution of MeMgI (3.0 M, *y* mol%) and diphenylacetylene (*x* equiv.). The reaction mixture was allowed to run at 80 °C for 24 h. At the end of reaction, the mixture was cooled to room temperature. GC standard *n*-dodecane (10 μ L) was added into the mixture. Aliquots of the reaction mixture were passed through a short plug of silica gel with EA washings. The filtrate was analyzed by GC for the calibrated yield of the product. For the purpose of recording NMR, the desired product (entry 3, Table 1.2) was purified by flash chromatography over silica gel using 25:1 hexanes/EA. The solvent was evaporated and replaced with CDCl₃.

Typical procedure for catalytic hydroarylation of alkynes: In the glovebox, a Schlenk tube containing a magnetic stir bar was charged with **1.34** (5 mol%, 7.4 mg), phosphine (20 mol%), arylpyridine (0.1 mmol) and THF (1 mL). To the mixture was added a THF solution of MeMgI (3.0 M, 0.2 mmol, 68 μ L) and alkyne (0.1 mmol). The reaction mixture was allowed to run at 80 °C for 24 h. At the end of reaction, the mixture was cooled to room temperature. For the purpose of recording NMR, the desired products were purified by flash chromatography over silica gel using 25:1 hexanes/EA. The solvent was evaporated and replaced with CDCl₃.

Typical procedure for catalytic Kumada cross-coupling reactions: In the glovebox, a 10-mL reaction tube containing a magnetic stir bar was charged with **1.34** (10 mol%, 14.8 mg) and aryl chloride (0.1 mmol). To the mixture was added a THF solution of MesMgBr (0.2 M, 0.2 mmol, 1 mL). The reaction mixture was allowed to run at 80 °C for 24 h. At the end of reaction, the mixture was cooled to room temperature. GC standard *n*-dodecane (10 µL) was added into the mixture. Aliquots of the reaction mixture were passed through a short plug of silica gel with EA washings. The filtrate was analyzed by GC for the determination of aryl chloride and the calibrated yield of the product. For the purpose of recording NMR, desired products were purified by flash chromatography over silica gel using hexanes. The solvent was evaporated and replaced with CDCl₃.

Diphenylacetylene (1.36a) Hydroarylation Products

1.37aa: Light yellow oil (45%). ^1H NMR (300 MHz, CDCl_3): δ 8.49-8.46 (m, 1H), 7.53-7.49 (m, 1H), 7.48-7.41 (m, 4H), 7.34-7.31 (m, 1H), 7.15-7.10 (m, 3H), 7.08-6.98 (m, 6H), 6.94-6.91 (m, 2H), 6.68 (s, 1H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 159.63, 148.96, 143.49, 142.43, 140.48, 140.22, 137.57, 135.34, 131.11, 130.88, 130.21, 129.22, 128.13, 127.87, 127.68, 126.73, 126.65, 124.35, 121.19 ppm.

1.37ba: Light yellow oil (54%). $\text{P}(4\text{-MeOC}_6\text{H}_4)_3$ was used instead of PPh_3 . ^1H NMR (300 MHz, CDCl_3): δ 8.46 (d, $J = 4.8$ Hz, 1H), 7.48-7.41 (m, 2H), 7.35-7.32 (m, 1H), 7.26-7.24 (m, 2H), 7.13-7.10 (m, 2H), 7.05-6.94 (m, 9H), 6.66 (s, 1H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 177.61, 176.85, 159.69, 149.02, 143.40, 142.66, 140.30, 137.98, 137.84, 137.72, 135.35, 131.62, 131.00, 130.33, 130.26, 129.30, 128.55, 127.96, 127.74, 126.80, 126.68, 124.46, 121.08, 21.28 ppm.

1.37ca: Light yellow oil (38%). ^1H NMR (300 MHz, CDCl_3): δ 8.45 (d, $J = 4.6$ Hz, 1H), 7.50-7.46 (m, 1H), 7.43-7.40 (m, 1H), 7.34-7.31 (m, 1H), 7.14-7.10 (m, 3H), 7.06-6.93 (m, 10H), 6.69 (s, 1H), 3.88 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 159.47, 159.35, 148.99, 144.89, 142.53, 139.99, 137.57, 135.34, 133.39, 131.60, 131.15, 130.30, 129.32, 127.99, 127.75, 126.89, 126.80, 124.50, 120.93, 116.49, 113.17, 55.51 ppm.

1.37da: Yellow oil (74%). $\text{P}(4\text{-MeOC}_6\text{H}_4)_3$ was used instead of PPh_3 ; ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[33] ^1H NMR (400 MHz, CDCl_3): δ 8.83 (dd, $J = 4.3$, 1.8 Hz, 1H), 8.05 (dd, $J = 8.0$, 1.8 Hz, 1H), 7.95 (dd, $J = 7.3$, 2.0 Hz, 1H), 7.84 (d, $J = 8.8$ Hz, 1H), 7.76-7.72 (m, 2H), 7.67 (d, $J = 8.8$ Hz, 1H), 7.38-7.34 (m, 3H), 7.30-7.28 (m, 2H), 7.26-7.16 (m, 3H), 7.19-7.02 (m, 3H), 6.68 (s, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 147.53, 147.35, 146.34, 142.99, 141.14, 138.80, 135.10, 134.97, 131.81, 130.77, 129.59, 128.30, 128.25, 127.96, 127.26, 127.18, 127.11, 126.43, 126.20, 125.92, 125.75, 121.10 ppm.

4-Octyne (1.36b) Hydroarylation Products

1.37ab: Colorless oil (38%). ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[33] ^1H NMR (300 MHz, CDCl_3): δ 8.69 (d, $J = 4.1$ Hz, 1H), 7.66-7.50 (m, 3H), 7.37-7.34 (m, 3.2 Hz, 2H), 7.26-7.19 (m, 2H), 5.49 (t, $J = 7.3$ Hz, 1H), 2.13-2.06 (m, 2H), 1.90-1.85 (m, 2H), 1.47-1.35 (m, 2H), 1.24-1.11 (m, 2H), 0.93 (t, $J = 7.3$ Hz, 3H), 0.73 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 159.85, 149.44, 143.55, 141.46, 138.65, 135.50, 131.84, 130.27, 129.93, 128.14, 126.94, 124.41, 121.51, 33.54, 30.46, 22.88, 21.69, 14.06, 14.02 ppm.

1.37bb: Light yellow oil (55%). $\text{P}(4\text{-MeOC}_6\text{H}_4)_3$ was used instead of PPh_3 . ^1H NMR (400 MHz, CDCl_3): δ 8.68-8.66 (m, 1H), 7.63-7.58 (m, 1H), 7.54-7.48 (m, 2H), 7.20-7.16 (m, 2H), 7.05 (s, 1H), 5.48 (t, $J = 7.3$ Hz, 1H), 2.40 (s, 3H), 2.09 (q, $J = 7.3$ Hz, 2H), 1.89-1.85 (m, 2H), 1.46-1.37 (m, 2H), 1.22-1.13 (m, 2H), 0.96-0.92 (m, 3H), 0.75-0.72 (m, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 159.86, 149.38, 143.40, 141.65, 137.86, 135.89, 135.42, 131.55, 130.93, 129.92, 127.69, 124.35, 121.29, 33.61, 30.47, 22.90, 21.74, 21.29, 14.11, 14.04 ppm.

1.37cb: Light yellow oil (33%). ^1H NMR (300 MHz, CDCl_3): δ 8.67-8.64 (m, 1H), 7.63-7.50 (m, 3H), 7.19-7.14 (m, 1H), 6.91 (dd, $J = 8.5, 2.7$ Hz, 1H), 6.79 (d, $J = 2.7$ Hz, 1H), 5.52 (t, $J = 7.3$ Hz, 1H), 3.87 (s, 3H), 2.10 (q, $J = 7.3$ Hz, 2H), 1.91-1.86 (m, 2H), 1.48-1.36 (m, 2H), 1.23-1.13 (m, 2H), 0.94 (t, $J = 7.4$ Hz, 3H), 0.74 (t, $J = 7.3$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 159.48, 159.39, 149.36, 145.02, 141.64, 135.44, 131.73, 131.50, 131.33, 124.26, 121.12, 116.07, 111.93, 55.40, 33.52, 30.43, 22.85, 21.73, 14.09, 14.03 ppm.

1.37db: Light yellow oil (57%). $\text{P}(4\text{-MeOC}_6\text{H}_4)_3$ was used instead of PPh_3 . ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[33] ^1H NMR (400 MHz, CDCl_3): δ 8.94 (dd, $J = 4.3, 1.9$ Hz, 1H), 8.14 (dd, $J = 8.0, 1.9$ Hz, 1H), 7.86-7.82 (m, 2H), 7.69-7.67 (m, 1H), 7.63-7.59 (m, 1H), 7.47-7.44 (m, 2H), 5.39 (t, $J = 7.3$ Hz, 1H), 2.88-2.81 (m, 1H), 2.42-2.35 (m, 1H), 2.30-2.20 (m, 2H), 1.63-1.57 (m, 2H), 1.29-1.23 (m, 2H), 1.10 (t, $J = 7.4$ Hz, 3H), 0.80 (t, $J = 7.3$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 147.55, 147.43, 147.04, 144.41, 135.15, 134.86, 131.08, 128.93, 128.66, 127.37, 127.31, 127.19, 125.54, 124.57, 120.83, 35.52, 30.45, 23.19, 22.03, 14.50, 14.10 ppm.

Kumada Cross-Coupling Products

1.40a: Colorless oil. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[36a] ^1H NMR (300 MHz, CDCl_3): δ 7.46-7.41 (m, 2H), 7.37-7.31 (m, 1H), 7.18-7.15 (m, 2H), 6.97 (s, 2H), 2.36 (s, 3H), 2.03 (s, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 141.11, 139.07, 136.55, 135.97, 129.31, 128.35, 128.04, 126.49, 21.02, 20.72 ppm. GCMS (EI) Calcd for $\text{C}_{15}\text{H}_{16}$: 196.1, found: 196.1.

1.40b: Colorless oil. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[36b] ^1H NMR (300 MHz, CDCl_3): δ 7.24 (d, $J = 7.7$ Hz, 2H), 7.05 (d, $J = 7.7$ Hz, 2H), 6.96 (s, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 2.03 (s, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 139.02, 138.01, 136.39, 136.14, 135.96, 129.16, 129.06, 128.02, 21.23, 21.01, 20.77 ppm. GCMS (EI) Calcd for $\text{C}_{16}\text{H}_{18}$: 210.1, found: 210.1.

1.40c: White solid. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[36c] ^1H NMR (300 MHz, CDCl_3): δ 7.06 (d, $J = 8.3$ Hz, 2H), 6.96 (m, 4H), 3.86 (s, 3H), 2.33 (s, 3H), 2.02 (s, 6H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 158.36, 138.83, 136.56, 133.47, 130.46, 128.16, 113.92, 55.35, 21.14, 20.92 ppm. GCMS (EI) Calcd for $\text{C}_{16}\text{H}_{18}\text{O}$: 226.1, found: 226.1.

1.40d: White solid. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[36d] ^1H NMR (300 MHz, CDCl_3): δ 7.70 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 6.97 (s, 2H), 2.36 (s, 3H), 2.00 (s, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 145.04, 137.61, 137.23, 135.61, 129.79, 128.24, 128.17, 125.39 (q, $J = 3.7$ Hz), 21.01, 20.64 ppm; ^{19}F NMR (282 MHz, CDCl_3): δ -62.38 ppm. GCMS (EI) Calcd for $\text{C}_{16}\text{H}_{15}\text{F}_3$: 264.1, found: 264.1.

1.40e: White solid. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[36e] ^1H NMR (300 MHz, CDCl_3): δ 7.13-7.11 (m, 4H), 6.96 (s, 2H), 2.35 (s, 3H), 2.01 (s, 6H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 161.71 (d, $J_{\text{C-F}} = 244.7$ Hz), 137.98, 136.87 (d, $J_{\text{C-F}} = 3.5$ Hz), 136.79, 136.13, 130.83 (d, $J_{\text{C-F}} = 7.8$ Hz), 128.11, 115.29 (d, $J_{\text{C-F}} = 21.1$ Hz), 20.99, 20.70 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -116.48 ppm. GCMS (EI) Calcd for $\text{C}_{15}\text{H}_{15}\text{F}$: 214.1, found: 214.1.

1.40f: Colorless oil. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[36f] ^1H NMR (400 MHz, CDCl_3): δ 7.31-7.28 (m, 1H), 7.27-7.23 (m, 2H), 7.04-7.02 (m, 1H), 6.96 (s, 2H), 2.36 (s, 3H), 2.00 (s, 3H), 1.94 (s, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 140.59, 138.22, 136.34, 135.88, 135.73, 129.90, 129.18, 128.00, 126.90, 125.99, 21.07, 20.22, 19.45 ppm. GCMS (EI) Calcd for $\text{C}_{16}\text{H}_{18}$: 210.1, found: 210.1.

1.5 Appendices

1.5.1. Crystallographic Data of All Crystal Structures

Compound	1.21	1.22	1.33	1.34
Formula	C ₆₁ H ₉₀ Cl ₃ Ir ₃ N ₄ Si ₂	C _{64.5} H ₉₄ Cl ₃ N ₄ Rh ₃ Si ₂	C ₆₀ H ₈₆ Cl ₄ N ₄ Rh ₄ Si ₂	C ₇₄ H ₁₀₈ Br ₄ Co ₂ N ₈ Si ₄
<i>M</i>	1618.49	1396.69	1472.96	1659.54
<i>T</i> / K	103(2)	296(2)	103(2)	103(2)
Color	Red	Yellow	Red	Black
Crystal size / mm	0.02 × 0.12 × 0.28	0.18 × 0.20 × 0.24	0.40 × 0.30 × 0.22	0.080 × 0.180 × 0.420
Crystal system	Triclinic	Triclinic	Triclinic	Orthorhombic
Space Group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> <i>b c a</i>
<i>a</i> / Å	12.7398(5)	12.6047(7)	10.07840(10)	14.1963(9)
<i>b</i> / Å	21.1659(10)	16.2646(8)	11.4261(2)	23.5360(16)
<i>c</i> / Å	24.7908(12)	18.0842(10)	13.5698(2)	23.8063(15)
<i>α</i> / °	100.510(3)	100.159(3)	98.1470(10)	90
<i>β</i> / °	103.594(3)	102.706(3)	90.3690(10)	90
<i>γ</i> / °	101.767(3)	109.288(3)	99.1060(10)	90
<i>V</i> / Å ³	6171.8(5)	3286.4(3)	1526.72(4)	7954.3(9)
<i>Z</i>	4	2	2	4
<i>d</i> _{calcd} / g cm ⁻³	1.742	1.411	1.602	1.386
<i>μ</i> / mm ⁻¹	6.662	0.943	1.317	2.531
<i>F</i> (000)	3176	1446	750	3432
Index ranges	-15 ≤ <i>h</i> ≤ 15	-18 ≤ <i>h</i> ≤ 18	-16 ≤ <i>h</i> ≤ 16	-19 ≤ <i>h</i> ≤ 19
	-25 ≤ <i>k</i> ≤ 25	-23 ≤ <i>k</i> ≤ 23	-19 ≤ <i>k</i> ≤ 18	-32 ≤ <i>k</i> ≤ 32
	-30 ≤ <i>l</i> ≤ 30	-26 ≤ <i>l</i> ≤ 26	-20 ≤ <i>l</i> ≤ 22	-31 ≤ <i>l</i> ≤ 33
No. of reflections collected	100829	150784	39554	157740
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2(<i>σ</i>)]	0.0635, 0.1128	0.0601, 0.1282	0.0317, 0.0796	0.0556, 0.0893
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1360, 0.1380	0.2067, 0.2023	0.0465, 0.0999	0.1085, 0.1040
Goodness-of-fit on <i>F</i> ²	1.025	0.962	1.112	1.075
Data / restraints / parameters	23505 / 2112 / 1453	21081 / 1447 / 950	14814 / 0 / 341	11185 / 169 / 468
Largest diff. peak and hole/ e Å ⁻³	3.054, -2.352	0.777, -0.952	1.268, -1.337	0.865 and -0.910

1.5.2. NMR Spectra of 1.34

Evans method:

¹H (395.9 MHz, C₆D₆, 24.0 °C):

1.5.3. NMR Spectra of New Products from 1.34-Catalyzed Hydroarylation of Alkynes

1.37aa: ^1H , ^{13}C

1.37ba: ^1H , ^{13}C

1.37ca: ^1H , ^{13}C

1.37bb: ^1H , ^{13}C

1.37cb: ^1H , ^{13}C

1.5.4. Theoretical Studies

Compound **1.34** was investigated using DFT B3LYP method with the 6-31G(d) basis set for Co and 6-311G(d) for other atoms. All calculations were carried out using the Gaussian 09 packages.^[37] The optimized geometries are in good agreement with their X-ray crystallographic data. NBO analysis, WBI, Laplacian distribution,^[38] Electron Location Function (ELF), spin density and spin population were performed at the same level of theory. Spin density = # of α electrons – # of β electrons. A positive spin density indicates that # of α electron are more than # of β electrons at some places and negative spin density indicates # of β electron are more than # of α electrons at other places. In the optimized B3LYP/6-31G(d) geometries, the harmonic vibrational frequency calculations were performed with the analytical force-constant matrix to verify the nature of the stationary points. That is, the local minimum (no imaginary frequencies) and the transition state (one imaginary frequency). In the same optimized geometries, higher-level single-point energy calculations were also performed, using the 6-311G(d) basis set. The relative energies for the dissociation of **1.34** are based on the differences of the free energies (ΔG ; kcal mol⁻¹) and enthalpies (ΔH ; kcal mol⁻¹) at B3LYP/6-311G(d)//B3LYP/6-31G(d) level of theory.

Table S1.1 Geometrical coordinates of **1.34** in its singlet state at B3LYP/6-31G(d).

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
35	-2.789813	0.939259	-1.977919
35	-3.235130	-0.483772	3.355495
6	-0.350914	-2.833760	-2.741308
6	0.182680	-1.483281	-3.244393
1	-0.398909	-0.650779	-2.843856
1	0.106972	-1.446393	-4.336731
1	1.228644	-1.331750	-2.967839
6	0.451180	-3.956717	-3.430546
1	1.495874	-3.954276	-3.105720
1	0.435254	-3.781218	-4.511843
1	0.031746	-4.948371	-3.251311
6	-1.841933	-2.951685	-3.115010
1	-2.261532	-3.907131	-2.783374
1	-1.961790	-2.892065	-4.203293
1	-2.411120	-2.132536	-2.666744
6	-0.232776	-3.857826	-0.384312
6	-0.250040	-5.316557	-0.719398
6	0.945132	-6.046577	-0.781842
1	1.888831	-5.548192	-0.589936
6	0.927510	-7.403076	-1.108089
1	1.861745	-7.955680	-1.155428
6	-0.282314	-8.045603	-1.377820
1	-0.294736	-9.101450	-1.633503
6	-1.476202	-7.324036	-1.317875
1	-2.422540	-7.816384	-1.524095
6	-1.461822	-5.967758	-0.990450
1	-2.392800	-5.414512	-0.935071
6	-0.080321	-3.973444	2.179476
6	1.381765	-4.419025	2.383066
1	1.660518	-5.211718	1.682005
1	1.510809	-4.812579	3.398293
1	2.055751	-3.568284	2.257751
6	-1.022554	-5.181024	2.358269
1	-2.060514	-4.907392	2.146402
1	-0.969566	-5.513459	3.401152
1	-0.748325	-6.029118	1.727395
6	-0.441892	-2.915556	3.231342
1	0.189484	-2.028992	3.132490
1	-0.288953	-3.328961	4.234511
1	-1.485619	-2.608180	3.144190
6	-5.131168	-2.519117	0.169578
6	-3.914772	-3.392972	0.507078
1	-3.052255	-3.120864	-0.106747

1	-4.156465	-4.446981	0.332314
1	-3.634862	-3.274902	1.558371
6	-6.319262	-2.986739	1.035358
1	-6.091820	-2.854355	2.098479
1	-6.514768	-4.050186	0.853597
1	-7.233966	-2.436715	0.801345
6	-5.458857	-2.660958	-1.330183
1	-6.397266	-2.165200	-1.590644
1	-5.557896	-3.721226	-1.592480
1	-4.659123	-2.224235	-1.935530
6	-5.432733	0.013885	0.439238
6	-6.797122	0.183793	-0.147871
6	-7.952490	0.069833	0.636472
1	-7.865667	-0.144349	1.697526
6	-9.212378	0.230605	0.056045
1	-10.103024	0.141724	0.671785
6	-9.326007	0.503803	-1.308291
1	-10.307048	0.627929	-1.758554
6	-8.175629	0.619403	-2.092837
1	-8.258247	0.835078	-3.154428
6	-6.914101	0.462142	-1.518181
1	-6.012656	0.559882	-2.116314
6	-4.925513	2.415389	1.145971
27	-1.436803	0.148974	-0.227913
7	-0.201016	-2.843402	-1.261400
7	-0.242332	-3.321968	0.849238
7	-4.744853	-1.136823	0.519392
7	-4.643801	0.980648	0.906497
14	-0.177998	-1.558530	0.154132
14	-3.163330	-0.230053	1.030691
35	2.484961	-0.785782	2.308843
35	3.597515	0.497843	-3.039983
6	0.346058	3.370234	2.255847
6	-0.142720	2.120480	3.005833
1	0.458674	1.243168	2.755519
1	-0.053333	2.284343	4.085375
1	-1.185450	1.893405	2.779184
6	-0.460292	4.590081	2.745858
1	-1.509255	4.521887	2.447672
1	-0.422774	4.613890	3.840630
1	-0.055662	5.536255	2.381323
6	1.837019	3.583277	2.578773
1	2.237216	4.463157	2.064112
1	1.970396	3.733289	3.656633
1	2.414385	2.702782	2.285871
6	0.263961	3.934813	-0.257709

6	0.231864	5.428520	-0.206163
6	-0.999255	6.100373	-0.171749
1	-1.921855	5.528730	-0.198711
6	-1.040086	7.492421	-0.097966
1	-1.999664	8.001342	-0.073352
6	0.146055	8.228865	-0.052098
1	0.112588	9.313144	0.008213
6	1.374105	7.566498	-0.084772
1	2.301020	8.132237	-0.050395
6	1.418337	6.173047	-0.163735
1	2.374534	5.661093	-0.193577
6	0.260545	3.546435	-2.798599
6	-1.045710	4.303516	-3.112161
1	-1.070342	5.295671	-2.654243
1	-1.134872	4.436409	-4.196679
1	-1.907566	3.723382	-2.768785
6	1.486621	4.389005	-3.201953
1	2.411687	3.837942	-3.007024
1	1.442070	4.604558	-4.275673
1	1.524333	5.344344	-2.671960
6	0.272625	2.239195	-3.606101
1	-0.633258	1.659750	-3.415810
1	0.310571	2.474982	-4.675728
1	1.148134	1.632339	-3.364655
6	5.276564	2.428090	0.162213
6	4.185656	3.366982	-0.378278
1	3.228842	3.191707	0.118881
1	4.481988	4.408491	-0.210356
1	4.046755	3.215978	-1.452616
6	6.573634	2.702837	-0.627823
1	6.430046	2.475758	-1.689400
1	6.844200	3.761368	-0.535338
1	7.412936	2.112998	-0.251697
6	5.498589	2.691305	1.665147
1	6.357956	2.134596	2.047516
1	5.688257	3.757859	1.834807
1	4.617911	2.397465	2.242513
6	5.409703	-0.129463	0.070829
6	6.692742	-0.366435	0.799236
6	7.922625	-0.435642	0.132230
1	7.962286	-0.301364	-0.944547
6	9.096945	-0.667988	0.851616
1	10.047049	-0.718711	0.327158
6	9.049834	-0.833476	2.237035
1	9.964518	-1.015333	2.794563
6	7.824104	-0.765785	2.904586

1	7.781142	-0.897207	3.982157
6	6.647840	-0.532609	2.191911
1	5.687547	-0.492687	2.698311
6	4.815544	-2.517171	-0.632394
6	5.897931	-2.757912	-1.706411
1	6.877610	-2.406673	-1.370252
1	5.983663	-3.830065	-1.919850
1	5.637931	-2.236804	-2.633394
6	5.185215	-3.233551	0.682004
1	4.485438	-2.958635	1.476514
1	5.134447	-4.318322	0.529394
1	6.198985	-2.994001	1.010983
6	3.481657	-3.077003	-1.147395
1	3.169222	-2.555001	-2.056420
1	3.600689	-4.139011	-1.388821
1	2.691251	-2.970743	-0.399443
27	1.389742	-0.071775	0.360098
7	0.177538	3.106914	0.799515
7	0.339561	3.167981	-1.359210
7	4.793820	1.052499	-0.085354
7	4.615344	-1.061754	-0.457109
14	0.193847	1.588108	-0.344021
14	3.223664	0.210983	-0.735995
6	-5.328728	3.159927	-0.143185
1	-4.592897	2.977461	-0.931646
1	-6.312214	2.851983	-0.505971
1	-5.373159	4.236888	0.059700
6	-3.626870	3.030564	1.684386
1	-3.786431	4.094692	1.890426
1	-3.325924	2.544495	2.616640
1	-2.811573	2.934124	0.960733
6	-6.017963	2.563014	2.226097
1	-6.985503	2.194612	1.874902
1	-5.737605	2.011467	3.129516
1	-6.140199	3.620485	2.488804

Table S1.2 Geometrical coordinates of **1.34** in its triplet state at B3LYP/6-31G(d).

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
35	-2.576480	-0.011211	-2.273660
35	-3.333497	-0.093923	3.415886
6	-0.234054	-3.676147	-2.549589
6	0.260779	-2.423009	-3.292789
1	-0.328395	-1.540369	-3.031887
1	0.165241	-2.581019	-4.372856
1	1.310722	-2.214348	-3.072257
6	0.631086	-4.872645	-2.992353
1	1.670117	-4.748981	-2.669352
1	0.624354	-4.919842	-4.086919
1	0.260678	-5.829238	-2.618272
6	-1.712109	-3.927644	-2.907797
1	-2.099630	-4.816885	-2.398992
1	-1.814945	-4.085891	-3.987792
1	-2.320088	-3.061629	-2.631246
6	0.026104	-4.204848	-0.031069
6	0.038447	-5.696189	-0.045110
6	1.246809	-6.394624	0.087065
1	2.176565	-5.844005	0.188223
6	1.257738	-7.789494	0.069340
1	2.200261	-8.321210	0.165929
6	0.063398	-8.499308	-0.072779
1	0.073080	-9.585656	-0.083465
6	-1.143437	-7.808225	-0.200755
1	-2.076434	-8.354554	-0.307636
6	-1.157312	-6.413239	-0.190939
1	-2.096813	-5.877366	-0.280945
6	0.278537	-3.718459	2.497071
6	1.760441	-3.948398	2.853401
1	2.166558	-4.819484	2.327931
1	1.864261	-4.125940	3.930312
1	2.351221	-3.064816	2.595741
6	-0.564875	-4.938816	2.915815
1	-1.605307	-4.828932	2.592199
1	-0.559859	-5.005768	4.009328
1	-0.175722	-5.881417	2.525508
6	-0.240716	-2.488400	3.261391
1	0.333148	-1.590379	3.019130
1	-0.146478	-2.664174	4.338821
1	-1.293219	-2.294484	3.040388
6	-4.963066	-2.540414	0.478277
6	-3.700092	-3.295062	0.924360
1	-2.866821	-3.091807	0.245407

1	-3.896805	-4.373122	0.923525
1	-3.404266	-3.002461	1.936680
6	-6.127634	-2.921517	1.415297
1	-5.899159	-2.635576	2.447271
1	-6.295003	-4.004723	1.383343
1	-7.058540	-2.432451	1.114752
6	-5.282516	-2.931534	-0.977844
1	-6.250532	-2.545463	-1.305305
1	-5.313875	-4.024273	-1.064518
1	-4.509585	-2.548391	-1.650542
6	-5.366762	-0.012967	0.291535
6	-6.661190	0.009086	-0.454126
6	-7.890121	-0.042101	0.216294
1	-7.911862	-0.092635	1.301005
6	-9.083808	-0.023623	-0.508476
1	-10.033295	-0.062712	0.018156
6	-9.055809	0.045294	-1.902429
1	-9.985380	0.059169	-2.464960
6	-7.830771	0.095857	-2.572922
1	-7.804148	0.148092	-3.657801
6	-6.634497	0.078537	-1.855517
1	-5.674987	0.112421	-2.365007
6	-4.962809	2.497265	0.635938
27	-1.298793	-0.012727	-0.184871
7	-0.121791	-3.392458	-1.093789
7	0.162612	-3.410192	1.046573
7	-4.657916	-1.099917	0.622534
7	-4.652555	1.051686	0.679595
14	0.011806	-1.855636	-0.008979
14	-3.160377	-0.039675	1.080226
35	2.544802	-0.004413	2.296705
35	3.371034	0.026293	-3.374527
6	0.246413	3.698137	2.491807
6	-0.269283	2.463767	3.252974
1	0.305068	1.567446	3.005731
1	-0.171636	2.635575	4.330709
1	-1.322282	2.269904	3.033769
6	-0.591506	4.917741	2.923525
1	-1.634019	4.814722	2.605185
1	-0.580007	4.976086	4.017473
1	-0.200778	5.861911	2.538621
6	1.730615	3.925579	2.840308
1	2.134373	4.796786	2.312879
1	1.841079	4.101991	3.916765
1	2.319290	3.041978	2.578239
6	-0.027133	4.193599	-0.033935

6	-0.053886	5.684663	-0.040700
6	-1.270698	6.367965	-0.173930
1	-2.195025	5.805900	-0.262729
6	-1.296757	7.762813	-0.172892
1	-2.245504	8.283148	-0.270469
6	-0.109463	8.487075	-0.045775
1	-0.130964	9.573305	-0.047795
6	1.105672	7.810818	0.083659
1	2.033066	8.368657	0.179285
6	1.134814	6.416087	0.090226
1	2.080421	5.891312	0.182393
6	-0.278861	3.670430	-2.554470
6	-1.761071	3.897208	-2.911175
1	-2.167140	4.770982	-2.390407
1	-1.865550	4.068657	-3.989051
1	-2.350974	3.014649	-2.648367
6	0.564835	4.884007	-2.991984
1	1.605913	4.777550	-2.669392
1	0.557290	4.936204	-4.086295
1	0.177300	5.832088	-2.613458
6	0.236659	2.428978	-3.303069
1	-0.336110	1.535233	-3.043080
1	0.135286	2.588453	-4.382396
1	1.290697	2.238363	-3.086083
6	4.953021	2.557315	-0.513279
6	3.696751	3.290665	-1.010197
1	2.851818	3.112593	-0.338920
1	3.891293	4.368377	-1.049226
1	3.419175	2.956532	-2.014786
6	6.129946	2.897540	-1.450659
1	5.915290	2.564870	-2.471474
1	6.295089	3.981437	-1.465735
1	7.057650	2.424709	-1.116369
6	5.253731	3.011140	0.928607
1	6.216290	2.637613	1.285630
1	5.286162	4.106536	0.969813
1	4.471328	2.658417	1.606946
6	5.368203	0.041232	-0.234887
6	6.662634	0.051421	0.510737
6	7.890961	0.055118	-0.162490
1	7.911678	0.050457	-1.248374
6	9.085475	0.065214	0.561244
1	10.034572	0.068258	0.032484
6	9.058643	0.071369	1.956805
1	9.988742	0.079189	2.518570
6	7.833973	0.067324	2.630140

1	7.808411	0.071765	3.716288
6	6.637114	0.057491	1.913873
1	5.678255	0.053650	2.425603
6	4.986446	-2.480991	-0.502076
6	6.167950	-2.816082	-1.435496
1	7.089890	-2.329701	-1.104695
1	6.345435	-3.898127	-1.440733
1	5.950467	-2.494982	-2.459442
6	5.290017	-2.918656	0.944127
1	4.504004	-2.565329	1.617974
1	5.331228	-4.013303	0.995583
1	6.249313	-2.534015	1.298121
6	3.738829	-3.232869	-0.993086
1	3.454448	-2.907348	-1.998603
1	3.947567	-4.308074	-1.027437
1	2.893485	-3.062685	-0.320205
27	1.291164	0.003965	0.193479
7	0.124751	3.397316	1.040237
7	-0.158642	3.382871	-1.100222
7	4.648675	1.112202	-0.594091
7	4.666533	-1.039942	-0.596946
14	-0.007138	1.844331	-0.022400
14	3.166822	0.025820	-1.039823
6	-5.171604	2.998515	-0.806221
1	-4.337839	2.684862	-1.440358
1	-6.098072	2.615705	-1.241147
1	-5.228041	4.093849	-0.813265
6	-3.749891	3.216930	1.247602
1	-3.940743	4.295361	1.283211
1	-3.564408	2.866944	2.267867
1	-2.847285	3.043206	0.653890
6	-6.201159	2.801005	1.504042
1	-7.105754	2.349211	1.088419
1	-6.056651	2.425337	2.522459
1	-6.362918	3.884321	1.554458

Table S1.3 Geometrical coordinates of **1.34A'** at B3LYP/6-31G(d).

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
35	1.427261	-0.020702	-2.560563
35	1.961125	-0.611207	3.418356
6	-3.372236	-1.665187	-2.624111
6	-2.298877	-0.932344	-3.447142
1	-1.286276	-1.240550	-3.169354
1	-2.436692	-1.150658	-4.511886
1	-2.369048	0.150425	-3.305250
6	-4.759421	-1.185415	-3.092161
1	-4.886873	-0.118108	-2.885415
1	-4.840900	-1.331893	-4.175218
1	-5.576707	-1.735427	-2.620668
6	-3.233880	-3.186528	-2.840784
1	-4.008892	-3.738181	-2.298498
1	-3.330116	-3.430845	-3.905305
1	-2.253393	-3.532721	-2.496756
6	-3.841856	-1.587740	-0.091803
6	-5.265706	-2.030323	-0.024927
6	-6.299558	-1.082992	0.011353
1	-6.056216	-0.024704	-0.010667
6	-7.632641	-1.492198	0.063910
1	-8.423669	-0.747920	0.091338
6	-7.948146	-2.852303	0.077318
1	-8.986180	-3.170766	0.115769
6	-6.924995	-3.802238	0.041810
1	-7.163810	-4.862108	0.054101
6	-5.591128	-3.395061	-0.006852
1	-4.797233	-4.135820	-0.023001
6	-3.238870	-1.354592	2.405248
6	-4.087072	-0.117593	2.765467
1	-5.086878	-0.176940	2.323763
1	-4.204966	-0.045319	3.852935
1	-3.600223	0.799454	2.417086
6	-3.923064	-2.639557	2.913855
1	-3.354388	-3.524702	2.607813
1	-3.960261	-2.622917	4.009117
1	-4.946990	-2.740079	2.547035
6	-1.861739	-1.236588	3.077379
1	-1.336726	-0.332437	2.759418
1	-1.980578	-1.190485	4.164950
1	-1.229793	-2.098789	2.842233

6	2.247248	-3.576008	0.430691
6	1.029183	-3.779856	1.350443
1	0.200297	-3.127263	1.056082
1	0.681558	-4.816091	1.276304
1	1.287172	-3.570202	2.393286
6	3.348224	-4.561494	0.870317
1	3.683352	-4.337190	1.889116
1	2.943282	-5.579782	0.861682
1	4.213747	-4.543553	0.204923
6	1.838379	-3.841018	-1.031978
1	2.693187	-3.750004	-1.708317
1	1.438548	-4.858042	-1.126869
1	1.070467	-3.132011	-1.354855
6	3.799203	-1.525291	0.244696
6	4.923323	-2.083026	-0.566131
6	6.057131	-2.635354	0.044692
1	6.122986	-2.670880	1.128145
6	7.093169	-3.148069	-0.737512
1	7.968673	-3.576116	-0.257197
6	7.003049	-3.111573	-2.130684
1	7.810597	-3.511004	-2.738228
6	5.874420	-2.559999	-2.741117
1	5.801118	-2.526305	-3.824545
6	4.833989	-2.044946	-1.965923
1	3.957759	-1.601144	-2.431883
6	4.578063	0.910926	0.573884
6	5.873966	0.622334	1.357335
1	6.464609	-0.168025	0.886589
1	6.493016	1.526435	1.389967
1	5.644186	0.325510	2.386275
6	4.895640	1.288123	-0.885820
1	3.972545	1.384336	-1.464048
1	5.430144	2.244980	-0.911819
1	5.526985	0.537297	-1.368946
6	3.841293	2.076880	1.256189
1	3.591973	1.828276	2.292883
1	4.477515	2.967847	1.256878
1	2.920034	2.329181	0.724416
27	0.262308	0.238025	-0.467526
7	-3.115930	-1.332510	-1.202060
7	-2.994913	-1.402842	0.946263
7	2.683284	-2.171200	0.621719
7	3.665831	-0.254852	0.651288

14	-1.544087	-1.071192	-0.197696
14	1.855848	-0.534437	1.063995
15	-0.401142	2.375304	-0.152535
6	-1.787437	2.842243	-1.294185
6	-1.618843	3.693049	-2.395125
6	-3.057519	2.282527	-1.071046
6	-2.689443	3.979996	-3.246815
1	-0.651206	4.140609	-2.592520
6	-4.130667	2.587249	-1.907792
1	-3.206523	1.613694	-0.228163
6	-3.949523	3.434901	-3.004192
1	-2.534618	4.639112	-4.097081
1	-5.110297	2.161273	-1.705018
1	-4.783739	3.667032	-3.660951
6	-1.070566	2.871315	1.502331
6	-2.137226	3.769440	1.673671
6	-0.431281	2.368740	2.646415
6	-2.564019	4.134198	2.952794
1	-2.639684	4.187058	0.807541
6	-0.851126	2.740730	3.924556
1	0.397962	1.676418	2.545517
6	-1.923006	3.620960	4.082266
1	-3.395177	4.826141	3.064071
1	-0.339974	2.332397	4.792156
1	-2.256052	3.906657	5.076748
6	0.844964	3.711900	-0.479620
6	0.997926	4.835470	0.347696
6	1.678961	3.585974	-1.605527
6	1.957189	5.808224	0.057355
1	0.371605	4.955635	1.225086
6	2.627156	4.567647	-1.900005
1	1.596850	2.708854	-2.242040
6	2.771369	5.680557	-1.068836
1	2.063861	6.668592	0.713311
1	3.259501	4.454174	-2.776780
1	3.515258	6.440264	-1.294951
1	3.259501	4.454174	-2.776780
1	3.515258	6.440264	-1.294951

Table S1.4 Geometrical coordinates of **1.34A''** at B3LYP/6-31G(d).

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
35	1.448495	-2.523648	-1.713319
35	0.900820	3.185166	0.180945
6	4.094493	1.223274	-1.656817
6	3.242011	1.855180	-2.773470
1	2.521462	1.132239	-3.172649
1	3.886272	2.177778	-3.597834
1	2.692894	2.726953	-2.402596
6	5.156796	2.239158	-1.193061
1	4.680946	3.148742	-0.811942
1	5.803639	2.513012	-2.034477
1	5.791286	1.820349	-0.406165
6	4.759368	-0.057381	-2.197585
1	5.468443	-0.482561	-1.482616
1	5.311790	0.178893	-3.114603
1	4.004264	-0.815035	-2.431573
6	3.302645	0.308423	0.628131
6	4.537151	-0.360525	1.132408
6	5.477693	0.346615	1.893120
1	5.305471	1.393230	2.127217
6	6.629702	-0.295268	2.351969
1	7.354873	0.258070	2.942024
6	6.847393	-1.641495	2.052870
1	7.744690	-2.139367	2.409949
6	5.911474	-2.347158	1.292454
1	6.079049	-3.393740	1.054350
6	4.757475	-1.713148	0.830735
1	4.029767	-2.251390	0.229096
6	1.604136	-0.242793	2.497059
27	0.167877	-0.585736	-1.507585
7	3.157421	0.942316	-0.544352
7	2.095497	0.320639	1.220356
14	1.295902	0.945636	-0.351034
6	-3.544256	2.341141	-0.756151
6	-2.572697	2.969010	-1.772033
1	-2.704247	2.526357	-2.765731
1	-2.765039	4.044628	-1.848726
1	-1.531604	2.838359	-1.462504
6	-3.319524	2.992351	0.622720
1	-2.291930	2.824577	0.960130
1	-3.483335	4.074198	0.555989

1	-4.010473	2.593948	1.371584
6	-4.987022	2.584073	-1.241692
1	-5.731371	2.237046	-0.520908
1	-5.146175	3.657642	-1.393934
1	-5.163359	2.077563	-2.197642
6	-3.933717	-0.155200	-0.232349
6	-5.120703	-0.105648	0.668304
6	-4.945825	0.147582	2.037056
1	-3.944898	0.303903	2.428406
6	-6.047984	0.194073	2.892845
1	-5.899041	0.386057	3.951736
6	-7.334795	-0.003384	2.389403
1	-8.192552	0.036677	3.054979
6	-7.516902	-0.252459	1.026722
1	-8.516314	-0.404485	0.628671
6	-6.417087	-0.307535	0.170712
1	-6.559860	-0.501656	-0.888069
6	-3.421511	-2.684778	-0.351597
6	-2.864067	-2.895332	1.071099
1	-3.458671	-2.353909	1.814792
1	-2.883190	-3.959503	1.333440
1	-1.826827	-2.549176	1.131315
6	-4.865877	-3.213928	-0.441716
1	-5.295353	-2.997713	-1.426167
1	-4.860116	-4.301422	-0.306527
1	-5.516241	-2.786597	0.324595
6	-2.554759	-3.455328	-1.363455
1	-1.515982	-3.110005	-1.351234
1	-2.558694	-4.523004	-1.119528
1	-2.943958	-3.333380	-2.380426
7	-3.223967	0.893939	-0.700152
7	-3.327224	-1.255121	-0.727315
14	-2.019064	-0.228465	-1.595405
6	1.699063	-1.781369	2.510528
1	1.234550	-2.202672	1.613019
1	2.737790	-2.120620	2.549038
1	1.183869	-2.178429	3.393210
6	0.125595	0.176087	2.602659
1	-0.291870	-0.176667	3.551687
1	0.023606	1.265116	2.559786
1	-0.465892	-0.257142	1.787891
6	2.378480	0.366027	3.681951
1	3.432479	0.076161	3.668335

1	2.315793	1.459361	3.659596
1	1.947037	0.014956	4.626366

Table S1.5 Geometrical coordinates of **PPh₃** at B3LYP/6-311G(d).

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
15	0.000000	0.000000	1.206691
6	0.000000	1.670133	0.402646
6	1.446377	-0.835066	0.402646
6	-1.446377	-0.835066	0.402646
6	-0.714326	1.995101	-0.761171
6	2.084971	-0.378926	-0.761171
6	-1.370645	-1.616175	-0.761171
6	0.745979	2.679646	1.035209
6	1.947652	-1.985859	1.035209
6	-2.693631	-0.693787	1.035209
6	-0.674286	3.290550	-1.282376
6	3.186843	-1.061326	-1.282376
6	-2.512556	-2.229224	-1.282376
6	0.795208	3.970618	0.508832
6	3.041052	-2.673979	0.508832
6	-3.836260	-1.296638	0.508832
6	0.082344	4.279991	-0.651853
6	3.665409	-2.211308	-0.651853
6	-3.747753	-2.068684	-0.651853
1	-1.307608	1.235168	-1.260668
1	1.723491	0.514838	-1.260668
1	-0.415883	-1.750005	-1.260668
1	1.287767	2.451955	1.950423
1	1.479572	-2.341216	1.950423
1	-2.767339	-0.110739	1.950423
1	-1.235670	3.525531	-2.183201
1	3.671035	-0.692644	-2.183201
1	-2.435365	-2.832887	-2.183201
1	1.380636	4.736852	1.010418
1	3.411916	-3.564092	1.010418
1	-4.792552	-1.172760	1.010418
1	0.111093	5.287602	-1.058148
1	4.523651	-2.740011	-1.058148
1	-4.634745	-2.547592	-1.058148

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CHAPTER 2:

An Amidinato Silicon(I)–Iron(II) Dimer: Synthesis and Hydroboration of Carbonyl Compounds

2.1 Introduction

Apart from C–H functionalization and C–C coupling reactions, the catalytic reduction of carbonyl compounds to alcohols poses itself as an important process for the synthesis of chemicals quintessential to our daily life. This transformation can be achieved by several methodologies, such as hydrosilylation, hydroboration, etc. As opposed to conventional hydrogenation, these synthetic strategies boast various advantages, not limited to non-hazardous, facile conditions and an overall operational convenience.^[1a] Moreover, these reactions can be tuned to yield high selectivity, tolerating other reducible groups including alkynes, ethers, esters and halides.^[1b,2] However, they tend to rely on catalysts bearing osmium, ruthenium, or other precious metals, which are scarce and costly.

On the account of affordability, iron complexes, likewise to other first-row transition metal species, have emerged as a suitable substitute in a variety catalytic processes.^[1] Being more sustainable, more economical, and less toxic, iron-based catalysts have gained considerable popularity amongst synthetic chemists. However, it is crucial to identify suitable ligand systems that can increase the thermal stability and reactivity of iron catalysts, while simultaneously avoiding one-electron pathways during catalysis.

Chart 2.1 Catalytically active iron complexes supported by (a) carbene; and (b) silylene ligands.

Over the years, a diverse class of competent catalysts has been established for the hydrosilylation of carbonyls. The range spans from simple salts,^[1] like [Fe(OAc)₂] (OAc = CH₃CO₂⁻) and [Fe(N(SiMe₃)₂)₂], to more elaborate systems commonly ligated by P- and/or N-donor pincer-type substances, for example porphyrin and diiminophosphine.^[3] Their redox-active nature grants efficient stabilization to the iron center and imparts selectivity to the catalysis, and is the reason they dominate this field. Nevertheless, carbene-supported iron species (Chart 2.1a), such as Royo's chelating cyclopentadienyl-*N*-heterocyclic (Cp-NHC) iron(II) chloride **2.1**, bis(NHC)-iron(II) chlorides **2.2** and **2.3** reported by the group of Glorius, are also catalytically active.^[4] Similarly, silylene-supported iron species (Chart 2.1b), for example hydrosilylene Fe(0) **2.4** and pincer-type Fe(0) **2.5**,^[5] have been successfully employed in catalytic hydrosilylation and, very recently, hydrogenation of carbonyl moieties with bis(silylenyl)-substituted ferrocene-stabilized η^6 -arene Fe(0) complex **2.6**.^[5] In the case of silylene-iron compounds,

an electron-rich Fe(0) center seems prevalent (**2.4** to **2.7**, Chart 2.1b), whereas Fe(II) appear common for their carbene analogues (**2.1** to **2.3**, Chart 2.1a).

With respect to hydroboration, since its discovery in 1956,^[6] the direct addition of B–H across unsaturated bonds has proven to be a versatile tool to access numerous organic intermediates.^[2] While organoboranes are of enormous significance in synthetic chemistry, catalytic hydroboration has only received due attention in the branch of C–C unsaturated bonds; progresses concerning C=O and C=N, on the other hand, have only emerged in recent times. There, now, exists an assortment of catalysts based on s-,^[7] p-,^[8] d-^[9] and even f-block^[10] elements capable of such transformations. A non-exhaustive list is illustrated in Chart 2.2.

Chart 2.2 Hydroboration catalysts based on (a) s-; (b) p-; (c) d-; and (d) f-block elements.

Surprisingly, examples based on iron only surfaced in literature starting from 2017, whereby the group of Findlater described a rather chemoselective reduction of aldehydes (vs. ketones) catalyzed by $[\text{Fe}(\text{acac})_3]$ (acac = acetylacetonate).^[9] It

should be noted that in the absence of reducing agent NaHBEt_3 , no catalysis was observed. For higher oxidation state or saturated iron complexes, an initial reduction to “Fe–H” is typical, and somewhat necessary, to commence the catalytic cycle. As proposed by the authors, $\text{Fe}(\text{acac})_3$ is first converted to an $[\text{Fe–H}]$ species which then interacts directly with an incoming molecule of carbonyl (Scheme 2.1).^[9] A metal alkoxide is formed upon insertion, and after σ -bond metathesis with pinacolborane (HBpin) eliminates the hydroborated product, regenerating the active $[\text{Fe–H}]$. An analogous process was suggested for a tin(II) species previously.^[8]

Scheme 2.1 Proposed mechanism for hydroboration of carbonyls catalyzed by $\text{Fe}(\text{acac})_3$ in the presence of NaHBEt_3 .

Following this inception, Baker and co-workers reported a hydroboration system exclusive to aldehydes accomplished by imine-coupled iron(II) complex (**2.8**, Chart 2.1c), and in the absence of any strong reducing agents due to the non-innocent ligand which potentially aids in the activation of HBpin .^[9]

Motivated by the collection of encouraging results, as well as those established in Chapter 1 with amidinato silicon(I) dimer $[\text{LSi:}]_2$ (**2.9**, $\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$)^[11] and group 9 transition metal complexes, we sought to develop an analogous system with iron. Herein, we report the synthesis of a base-stabilized silicon(I)–iron(II) dimer and its catalytic hydroboration of carbonyl compounds in the absence of any strong reducing agents.

2.2 Results and Discussion

2.2.1. Synthesis of Amidinato Silicon(I)–Iron(II) Dimer (**2.10**)

Treatment of **2.9** with FeBr₂ in THF at ambient temperature afforded the silicon(I)–iron(II) dimer [LSi(FeBr₂•thf)]₂ (**2.10**, Scheme 2.2) after 40 hours. Remarkably, the Si–Si σ -bond was not cleaved as in the case with CoBr₂ (see Chapter 1 for details). It is presumed that **2.9** acts as a Lewis base to coordinate to Lewis acidic anhydrous FeBr₂, together with the concomitant donation of electron density by a THF molecule, to generate the product. It should be noted that reducing the reaction time (ca. 16 hours) or employing equimolar FeBr₂ only compromised the yield of **2.10** (50%, Scheme 2.2) with recovery of precursor **2.9**. This suggests that any mononuclear adduct, even if formed, cannot be isolated.

Scheme 2.2 Synthesis of silicon(I)–iron(II) dimer **2.10**.

Single crystal XRD was used to characterize **2.10** (Figure 2.1). The silicon–iron interactions (Si1–Fe1: 2.508(3), Si2–Fe2: 2.490(3) Å) coincide well with other silylene-Fe(II) complexes (Chart 2.3a).^[5] Furthermore, they are considerably elongated with respect to related compounds bearing iron in a formal oxidation state of zero (Chart 2.3b), in which the latter are shortened on the basis of π -back bonding from the electron-rich Fe(0) centers to the Si atoms,^[5] and suggests that the Fe centers of **2.10** are in +2 oxidation states. Si1–Si2 in **2.10** measures

2.407(4) Å, which is only marginally shortened compared to its precursor (2.413(2) Å).^[11] A similar observation was noted when heavier analogue amidinato germanium(I) dimer [LGe:]₂ (L = PhC(NtBu)₂) reacted with Fe₂(CO)₉ to generate [L{Fe(CO)₄}Ge]₂, whereby the retained Ge–Ge bond is only reduced slightly from its original length (2.57(5) to 2.55(5) Å).^[13] Other resemblances between the abovementioned reactivities include the addition of iron moieties in a *gauche*-bent fashion by the loss of stereogenic lone pairs on the heavier group 14 element(I) atoms. The resulting Si and Fe centers in **2.10** are all four-coordinate and adopt tetrahedral geometries, albeit with that around silicon experiencing a greater degree of distortion.

Figure 2.1 ORTEP drawing of **2.10** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules are elided for clarity. Selected bond lengths (Å) and bond angles (°): Si1–Si2 2.407(4), Si1–Fe1 2.508(3), Si2–Fe2 2.490(3); Br2–Fe1–Si1 114.93(11), Si1–Fe1–Br1 106.18(10), Br1–Fe1–O1 101.9(6), O1–Fe1–Br2 100.4(4), Fe1–Si1–N1 113.5(3), N1–Si1–N2 71.1(4), N2–Si1–Si2 107.7(3), Si2–Si1–Fe1 127.14(15).

(a)

Si-Fe:
2.4923(4), 2.4823(4) (X = Cl)
2.498(8), 2.504(8) (X = Br)

Si-Fe: 2.5256(7), 2.5110(7)

(b)

Si-Fe:
2.237(7) (X = OtBu)
2.2777(5) (X = P(SiMe₃)₃)
2.2412(7) (X = PH₂)
2.2307(10) (X = PH₂(W(CO)₅)
2.2917(9) (X = PH(Pt(H)(PPh₃)₂))

Si-Fe: 2.229(11)

Si-Fe:
2.1782(16) (R = H)
2.1752(8), 2.1707(8) (R = Me)

Si-Fe:
2.1634(9) (X = Cl)
2.200(2) (X = Me)
2.184(2) (X = H)

Si-Fe:
2.1637(15), 2.1695(13) (X = (PMe₃)₂)
2.1579(15), 2.1664(15) (X = (CO)₃)

Chart 2.3 Structures and Si-Fe bond lengths (Å) of (a) silylene-Fe(II); and (b) silylene-Fe(0) complexes.

Paramagnetism is characteristic of Fe(II) complexes such as **2.10**; this trait is reflected by its silence in NMR spectroscopies. The effective magnetic moment (μ_{eff}) of **2.10** was determined, by Evans method, to be 6.47 μB in THF-*d*₈. Although higher than those described for monoiron carbene complexes^[14] and four-coordinated high-spin iron phosphine complexes,^[15] this value is lower than that anticipated for a system bearing two uncoupled high-spin Fe centers.^[16] This is an indication that some degree of antiferromagnetic coupling exists between the two iron centers in **2.10**. A similar observation was reported for chloride-bridged diiron complex $[\text{Fe}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{IMes})_2]$ (IMes = {HCN(2,4,6-Me₃C₆H₂)}₂C:), which exhibits a μ_{eff} of 6.5(1) BM.^[14]

2.2.2. Catalytic Hydroboration of Ketones by Amidinato Silicon(I) Dimer-Iron(II) (**2.10**)

In comparison with hydrosilylation, the underdevelopment of iron-catalyzed hydroboration prompted us to focus our efforts in this arena. Condition optimization was conducted with acetophenone (**2.11a**) and HBpin, which was selected on the foundation of its practicality and versatility. Brief solvent screening (entries 1 to 4, Table 2.1) with 3 mol% of **2.10** as catalyst and equimolar HBpin suggested acetonitrile and toluene to be relatively superior (entries 2 and 3) at room temperature over 16 hours. Although both produced similar levels of substrate conversion (61 vs. 63% respectively), when the amount of **2.10** and HBpin increased, toluene was outperformed by acetonitrile (entry 9 vs. 7). This could be ascribed to poor solubility of catalyst **2.10** in toluene. Through a further evaluation of catalyst and hydroborating agent loadings, we surmised that a reaction with 1.5 equivalents of HBpin and 10 mol% of **2.10** in acetonitrile afforded the best results (entry 7). Insignificant conversion occurred in the absence of **2.10** (entry 1, Table S2.1, see section 2.5.1) and was only achieved at sub-standards when salts of FeBr₂ (entries 3 and 4, Table S2.3) and FeBr₂•thf₂ (entries 5 and 6) were employed, highlighting that presence of amidinato silicon(I) dimer (**2.9**) in **2.10** plays a crucial role in activating possible catalytic intermediates.

Table 2.1 Condition optimization for hydroboration of acetophenone.

Entry	HBpin (equiv.)	2.10 (mol%)	Solvent	Conversion (%) ^a
1	1	3	THF	42
2	1	3	MeCN	61
3	1	3	toluene	63
4	1	3	dioxane	35
5	1	5	MeCN	71
6	1	10	MeCN	90
7	1.5	10	MeCN	97
8	2	10	MeCN	96
9	1.5	10	toluene	90

^a Determined by GC with *n*-dodecane as internal standard; based on **2.11a**.

With the optimized condition in hand, we proceeded to evaluate the scope of the reaction (Chart 2.4). Both electron-donating (**2.12b,c**) and electron-withdrawing (**2.12d,e**) groups on the aryl rings of the ketone were tolerated. 3-Acetylthiophene (**2.11f**) could also react well and led to the desired product **2.12f** in 95% yield. Aliphatic ketone, 3-methyl-2-butanone (**2.11k**), was also converted smoothly by this methodology. It should be noted that the reaction of propiophenone (**2.11h**) with HBpin led to product **2.12h** in only 60% yield, and the use of benzophenone (**2.11i**) did not lead to proposed product due to steric effect.

Chart 2.4 Scope of ketone hydroboration mediated by **2.10**.^a

^a Reactions were performed under conditions stated in Table 2.1, entry 7; GC-conversions are accounted.

Interestingly, we noted that no reducing agent was required to evoke catalysis. In light of this phenomenon, we probed the mechanism for **2.10**-catalyzed hydroboration by treating **2.10** with a stoichiometric amount of HBpin. No reaction was detected over the course of 16 hours, as monitored by ¹¹B NMR spectroscopy, suggesting that the first step of the catalytic cycle should involve **2.10** and carbonyl substrates exclusively.

Moreover, a combination of **2.9** (10 mol%) and FeBr₂•thf₂ (20 mol%) could accomplish the catalytic hydroboration of a series of aromatic and non-aromatic ketones, as well as a range of aldehydes **2.13** (Chart 2.5). This modified protocol is found to be capable of overcoming steric constraints, affording 90% conversion to **2.12h** (previously 60%) and 13% conversion to **2.12i** (previously not detected), indicating that carbonyls could insert into the Si–Fe bonds during **2.10**-catalyzed hydroboration. Exclusive selectivity for the carbonyl functionality over olefins (**2.11l** and **2.13m**) and esters (**2.13n**) was also observed.

Chart 2.5 Scope of carbonyl hydroboration mediated by **2.9** and $\text{FeBr}_2 \cdot \text{thf}_2$.^a

^a GC-conversion determined with *n*-dodecane as internal standard based on carbonyl starting material is reported. ^b Catalytic loading for ketone substrates: **2.9** (10 mol%), $\text{FeBr}_2 \cdot \text{thf}_2$ (20 mol%).

In this context, it is proposed that the carbonyl compounds insert into the Si–Fe bonds of **2.10** to form zwitterionic intermediate **2.10A** in the first step of the catalysis (Scheme 2.3). There is another possibility that **2.10** could dissociate into **2.9** and $\text{FeBr}_2 \cdot \text{thf}_x$ during the catalysis, which then function as Lewis base and Lewis acid respectively to react with carbonyl substrates to form **2.10A**. Subsequent reaction with HBpin proffers the corresponding boron esters and regenerates **2.10**. Such a mechanism is not known in both silicon and iron chemistry as yet.

Scheme 2.3 Proposed catalytic cycle for the hydroboration of carbonyl compounds mediated by silicon(I)–iron(II) complex **2.10**.

2.3 Conclusion

The amidinato silicon(I) dimer (**2.9**) reacted with FeBr_2 with a surprising retention of the Si–Si σ -bond to yield product diiron complex **2.10**. The latter was found to be catalytically active in the hydroboration of carbonyls without the addition of any strong reducing agents. Mechanistic studies showed that carbonyl compounds could be inserted into the Si–Fe bonds of **2.10**, followed by reaction with HBpin to form boron esters. Isolation of reaction intermediates in the catalysis are still underway.

2.4 Experimental

2.4.1. Synthesis of 2.10

General considerations: All manipulations, unless otherwise stated, were carried out by using standard Schlenk and glovebox techniques under an atmosphere of high purity argon. THF was dried and distilled over molten potassium. The Evans NMR spectrum of **2.10** was acquired on a Jeol ECA 400 spectrometer. All chemicals were used as received, unless stated otherwise. **2.9** was synthesized by the procedure outlined in section 1.4.1.

X-ray data collection and structural refinement: Intensity data for compound **2.10** was collected by using a Bruker APEX II diffractometer. Reflections were measured at 133(2) K. The structure was solved by direct-phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2 .^[17] All nonhydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations.

Synthesis of 2.10: THF (20 mL) was added to a mixture of **2.9** (0.2588 g, 0.499 mmol, 1.0 equiv.) and FeBr₂ (0.2157 g, 1.000 mmol, 2.0 equiv.) at ambient temperature. The mixture was allowed to stir for 40 hours. Upon filtration and concentration, orange crystals of **2.10** were obtained.

Yield: 0.31 g (50%); M.p. 148 °C (dec).

Elemental analysis calcd (%) for C₃₈H₆₂Br₄Fe₂N₄O₂Si₂: C 41.70, H 5.71, N 5.12; found: C 41.01, H 5.74, N 5.27.

$\mu_{\text{eff}} = 6.47 \mu\text{B}$ (Evans method, see section 2.5.2 for NMR spectrum).

Crystallographic data: C₄₆H₇₈Br₄Fe₂N₄O₄Si₂; $M = 1238.64$; triclinic $P \bar{1}$; $a = 10.9129(5)$, $b = 11.1666(5)$, $c = 24.2842(8)$ Å; $\alpha = 100.844(3)^\circ$, $\beta = 92.910(3)^\circ$, $\gamma = 106.999(3)^\circ$; $V = 2761.8(2)$ Å³; $Z = 2$; $d_{\text{calcd}} = 1.489$ g cm⁻³; $\mu = 3.504$ mm⁻¹; $F(000) = 1268$; $-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $0 \leq l \leq 29$; 9992 reflections collected; $R1 = 0.0757$, $wR2 = 0.1501$ ($I > 2(\sigma)I$); $R1 = 0.1537$, $wR2 = 0.1876$ (all data).

2.4.2. Catalytic Studies

General considerations: All glassware were dried at 120 °C prior to use; an argon-filled glovebox was used when required. Toluene was dried using a MBraun Solvent purification system; THF was dried over molten potassium; dioxane was dried over CaH_2 ; anhydrous acetonitrile was purchased from Kanto and used directly. All NMR spectra were acquired on Bruker 500 MHz, 400 MHz, or 300 MHz or Jeol ECA 400 MHz NMR spectrometers. ^1H NMR chemical shifts were recorded relative to TMS (δ 0.00) or residual solvent peaks. All chemicals were used as received, unless stated otherwise. GC internal standard, *n*-dodecane, was degassed with argon and dried over activated 4 Å molecular sieve beads before use. Flash chromatography was performed using Merck 40-63D 60 Å silica gel. GC analysis was performed on a Shimadzu GC-2010 instrument with Agilent J & W GC column DB-5MS-UI. GC/MS analysis was conducted on a Thermo Scientific DSQ II single quadrupole GC/MS instrument with Agilent J & W GC column DB-5MS-UI. Proof of purity of new compounds was demonstrated with copies of ^1H , ^{11}B , ^{13}C and ^{19}F NMR spectra (see section 2.5.3).

Typical procedure for condition optimization for catalytic hydroboration of acetophenone: In the glovebox, a 10-mL reaction tube containing a magnetic stir bar was charged with catalyst (*y* mol%), acetophenone (12.0 mg, 0.1 mmol), HBpin (*x* equiv.) and solvent (0.2 mL). The tube was capped tightly and the reaction mixture was allowed to run at room temperature for 16 h. At the end of reaction, GC standard *n*-dodecane (10 µL) was added into the mixture. Aliquots of the reaction mixture were passed through a short plug of silica gel with EA washings. The filtrate was analyzed by GC for the determination of conversion of acetophenone.

Typical procedure for condition optimization for catalytic hydroboration of benzaldehyde: In the glovebox, a 10-mL reaction tube containing a magnetic stir bar was charged with catalyst (*x* mol%), additive (*y* mol%), benzaldehyde (10.6 mg, 0.1 mmol), HBpin (12.8 mg, 0.1 mmol) and MeCN (0.5 mL). The tube was capped tightly and the reaction mixture was allowed to run at room temperature for 15 min. At the end of reaction, GC standard *n*-dodecane (10 µL) was added into the mixture. Aliquots of the reaction mixture were passed through a short plug of silica gel with EA washings. The filtrate was analyzed by GC for the determination of conversion of benzaldehyde.

Typical procedure for catalytic hydroboration of ketones mediated by 2.10: In the glovebox, a 10-mL reaction tube containing a magnetic stir bar was charged with **2.10** (10 mol%, 10.9 mg), ketone (0.1 mmol), HBpin (19.2 mg, 0.15 mmol) and MeCN (0.2 mL). The tube was capped tightly and the reaction mixture was allowed to run at room temperature for 16 h. Upon completion of reaction, GC standard *n*-dodecane (10 μ L) was added into the mixture. Aliquots of the reaction mixture were passed through a short plug of silica gel with EA washings. The filtrate was analyzed by GC for the determination of conversion of ketone. For the purpose of recording NMR, volatiles were removed using a high-vacuum Schlenk line after the reaction. The desired product was dissolved in *n*-hexane and filtered through celite. The solvent was evaporated and replaced with C₆D₆.

Typical procedure for catalytic hydroboration of carbonyl compounds mediated by 2.9 and FeBr₂•thf₂: In the glovebox, a 10-mL reaction tube containing a magnetic stir bar was charged with **2.9** (5 mol%), FeBr₂•thf₂ (10 mol%), and aldehyde (0.1 mmol), or **2.9** (10 mol%), FeBr₂•thf₂ (20 mol%), and ketone (0.1 mmol), HBpin (12.8 mg, 0.1 mmol) and MeCN (0.5 mL). The tube was capped tightly and the reaction mixture was allowed to run at room temperature for 12 h. Upon completion of reaction, GC standard *n*-dodecane (10 μ L) was added into the mixture. Aliquots of the reaction mixture were passed through a short plug of silica gel with EA washings. The filtrate was analyzed by GC for the determination of conversion of carbonyl. For the purpose of recording NMR, volatiles were removed using a high-vacuum Schlenk line after the reaction. The desired product was dissolved in *n*-hexane and filtered through celite. The solvent was evaporated and replaced with C₆D₆.

Ketone Hydroboration Products

2.12a: ^1H , $^{11}\text{B}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[18] ^1H NMR (300 MHz, C_6D_6): δ 7.38-7.36 (m, 2H), 7.12-7.07 (m, 2H), 7.05-7.03 (m, 1H), 5.42 (q, J = 6.4 Hz, 1H), 1.46 (d, J = 6.4 Hz, 3H), 1.03 (s, 6H), 1.00 (s, 6H) ppm; ^{11}B NMR (96 MHz, C_6D_6): δ 22.68 ppm; ^{13}C NMR (100 MHz, C_6D_6): δ 145.04, 128.19, 127.00, 125.34, 82.17, 72.62, 25.42, 24.33, 24.31 ppm.

2.12b: ^1H NMR (400 MHz, C_6D_6): δ 7.32 (d, J = 7.8 Hz, 2H), 6.98 (d, J = 7.7 Hz, 2H), 5.45 (q, J = 6.4 Hz, 1H), 2.09 (s, 3H), 1.50 (d, J = 6.4 Hz, 3H), 1.03 (s, 6H), 1.01 (s, 6H) ppm; ^{11}B NMR (96 MHz, C_6D_6): δ 22.80 ppm; ^{13}C NMR (75 MHz, C_6D_6): δ 142.30, 136.39, 129.00, 125.48, 82.27, 72.64, 25.58, 24.52, 24.45, 20.86 ppm.

2.12c: ^1H , $^{11}\text{B}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[8] ^1H NMR (300 MHz, C_6D_6): δ 7.31 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 5.43 (q, J = 6.3 Hz, 1H), 3.29 (s, 3H), 1.50 (d, J = 6.4 Hz, 3H), 1.04-1.02 (m, 12H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.54 ppm; ^{13}C NMR (100 MHz, C_6D_6): δ 159.05, 137.17, 126.65, 113.69, 82.14, 72.33, 54.53, 25.44, 24.42, 24.33 ppm.

2.12d: ^1H NMR (400 MHz, C_6D_6): δ 7.31 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.3 Hz, 2H), 5.27 (q, J = 6.4 Hz, 1H), 1.32 (d, J = 6.5 Hz, 3H), 1.02 (s, 6H), 0.99 (s, 6H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.50 ppm; ^{13}C NMR (100 MHz, C_6D_6): δ 148.77, 129.11 (q, $J_{\text{C-F}}$ = 32.0 Hz), 125.58, 125.14 (q, $J_{\text{C-F}}$ = 3.8 Hz), 124.67 (q, $J_{\text{C-F}}$ = 271.7 Hz), 82.43, 71.91, 25.13, 24.29, 24.25 ppm; ^{19}F NMR (376 MHz, C_6D_6): δ -62.09 ppm.

2.12e: ^1H NMR (400 MHz, C_6D_6): δ 7.85 (s, 1H), 7.62-7.60 (m, 3H), 7.48 (d, J = 8.5 Hz, 1H), 7.24-7.22 (m, 2H), 5.59 (q, J = 6.4 Hz, 1H), 1.55 (d, J = 6.5 Hz, 3H), 1.03 (s, 6H), 1.00 (s, 6H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.71 ppm; ^{13}C NMR (100 MHz, C_6D_6): δ 142.46, 133.61, 133.05, 128.10, 125.85, 125.48, 123.93, 123.89, 82.26, 72.77, 25.40, 24.36, 24.27 ppm.

2.12f: ^1H NMR (500 MHz, C_6D_6): δ 7.00 (s, 1H), 6.96-6.95 (m, 1H), 6.88-6.86 (m, 1H), 5.45 (q, J = 6.1 Hz, 1H), 1.44 (d, J = 6.1 Hz, 3H), 1.03 (s, 6H), 1.02 (s, 6H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.66 ppm; ^{13}C NMR (100 MHz, C_6D_6): δ 146.19, 125.62, 125.49, 120.01, 82.19, 69.13, 36.75, 24.35, 24.26 ppm.

2.12h: ^1H NMR (300 MHz, C_6D_6): δ 7.37 (d, J = 7.3 Hz, 2H), 7.12-7.03 (m, 3H), 5.22 (t, J = 6.3 Hz, 1H), 1.87-1.72 (m, 2H), 1.02 (s, 6H), 0.99 (s, 6H), 0.89 (t, J = 7.4 Hz, 3H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.61 ppm; ^{13}C NMR (75 MHz, C_6D_6): δ 143.92, 127.15, 126.03, 82.27, 77.93, 32.30, 24.41, 24.35, 9.81 ppm.

2.12i: ^1H , $^{11}\text{B}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[18] ^1H NMR (400 MHz, C_6D_6): δ 7.47-7.44 (m, 4H), 7.11-7.07 (m, 4H), 7.02-7.00 (m, 2H), 6.45 (s, 1H), 0.98 (s, 12H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.83 ppm; ^{13}C NMR (75 MHz, C_6D_6): δ 144.15, 128.89, 127.88, 127.26, 83.19, 78.80, 25.01 ppm.

2.12j: ^1H , $^{11}\text{B}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[18] ^1H NMR (400 MHz, C_6D_6): δ 4.26-4.22 (m, 1H), 1.92-1.90s (m, 2H), 1.62-1.60 (m, 2H), 1.54-1.45 (m, 2H), 1.30-1.23 (m, 2H), 1.17-1.12 (m, 2H), 1.08 (s, 12H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.40 ppm; ^{13}C NMR (100 MHz, C_6D_6): δ 81.86, 72.41, 34.43, 25.41, 24.41, 23.77 ppm.

2.12k: ^1H NMR (300 MHz, C_6D_6): δ 4.20-4.12 (m, 1H), 1.72-1.63 (m, 1H), 1.17 (d, J = 6.3 Hz, 3H), 1.07 (s, 12H), 0.93 (d, J = 6.7 Hz, 3H), 0.87 (d, J = 6.8 Hz, 3H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.51 ppm; ^{13}C NMR (100 MHz, C_6D_6): δ 81.84, 75.17, 34.43, 24.37, 24.33, 19.32, 18.08, 17.62 ppm.

2.12l: ^1H , $^{11}\text{B}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[18] ^1H NMR (300 MHz, C_6D_6): δ 5.98-5.94 (m, 1H), 5.68-5.64 (m, 1H), 4.84-4.82 (m, 1H), 1.83-1.74 (m, 2H), 1.68-1.62 (m, 2H), 1.38-1.31 (m, 2H), 1.07 (s, 12H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.51 ppm; ^{13}C NMR (100 MHz, C_6D_6): δ 130.42, 130.00, 82.65, 68.67, 31.63, 25.48, 25.14, 19.71 ppm.

Aldehyde Hydroboration Products

2.14a: ^1H , $^{11}\text{B}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[18] ^1H NMR (300 MHz, C_6D_6): δ 7.33-7.31 (m, 2H), 7.13-7.11 (m, 2H), 7.08-7.03 (m, 1H), 4.96 (s, 2H), 1.04 (s, 12H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.83 ppm; ^{13}C NMR (100 MHz, C_6D_6): δ 139.70, 128.24, 127.22, 126.70, 82.38, 66.63, 24.37 ppm.

2.14b: ^1H , $^{11}\text{B}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[18] ^1H NMR (400 MHz, C_6D_6): δ 7.25 (d, $J = 7.8$ Hz, 2H), 6.97 (d, $J = 7.8$ Hz, 2H), 4.94 (s, 2H), 2.09 (s, 3H), 1.05 (s, 12H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.78 ppm; ^{13}C NMR (100 MHz, C_6D_6): δ 137.40, 137.27, 129.61, 127.56, 83.01, 67.23, 25.08, 21.46 ppm.

2.14c: ^1H , $^{11}\text{B}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[18] ^1H NMR (400 MHz, C_6D_6): δ 7.24-7.16 (m, 2H), 6.74-6.61 (m, 2H), 4.90 (s, 2H), 3.31 (s, 3H), 1.06 (s, 12H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.67 ppm; ^{13}C NMR (100 MHz, C_6D_6): δ 159.95, 132.40, 129.20, 114.42, 83.02, 67.08, 55.30, 25.06 ppm.

2.14d: ^1H NMR (400 MHz, C_6D_6): δ 7.29 (d, $J = 8.2$ Hz, 2H), 7.07 (d, $J = 7.7$ Hz, 2H), 4.79 (s, 2H), 1.04 (s, 12H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.74 ppm; ^{13}C NMR (100 MHz, C_6D_6): δ 144.20, 129.99 (q, $J_{\text{C-F}} = 32.0$ Hz), 127.20, 125.80 (q, $J_{\text{C-F}} = 3.7$ Hz), 125.37 (q, $J_{\text{C-F}} = 270.3$ Hz), 83.33, 66.37, 24.99 ppm; ^{19}F NMR (376 MHz, C_6D_6): δ -62.08 ppm.

2.14e: ^1H NMR (400 MHz, C_6D_6): δ 7.77 (br, 1H), 7.60 (br, 3H), 7.40-7.37 (m, 1H), 7.23 (br, 2H), 5.10 (s, 2H), 1.06 (s, 12H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.92 ppm; ^{13}C NMR (100 MHz, C_6D_6): δ 137.76, 134.21, 133.68, 126.61, 126.30, 126.00, 125.60, 83.11, 67.41, 25.13 ppm.

2.14f: ^1H NMR (400 MHz, C_6D_6): δ 6.97-6.88 (m, 3H), 4.86 (s, 2H), 1.04 (s, 12H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.65 ppm; ^{13}C NMR (100 MHz, C_6D_6): δ 141.44, 127.39, 126.41, 122.55, 83.07, 63.01, 25.07 ppm.

2.14g: ^1H , $^{11}\text{B}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ spectra are identical to those reported in the literature.^[19] ^1H NMR (400 MHz, C_6D_6): δ 6.83 (br, 2H), 6.67 (br, 1H), 5.00 (s, 2H), 1.04 (s, 12H) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ 22.76 ppm; ^{13}C

NMR (100 MHz, C₆D₆): δ 143.14, 127.13, 126.39, 126.02, 83.22, 62.21, 25.10 ppm.

2.14m: ¹H, ¹¹B{¹H} and ¹³C{¹H} spectra are identical to those reported in the literature.^[20] ¹H NMR (400 MHz, C₆D₆): δ 5.40-5.35 (m, 2H), 3.60-3.50 (m, 2H), 1.80-1.48 (m, 6H), 1.05-0.96 (m, 1H), 0.83 (s, 12H) ppm; ¹¹B NMR (128 MHz, C₆D₆): δ 22.50 ppm; ¹³C NMR (100 MHz, C₆D₆): δ 127.47, 126.63, 82.71, 70.01, 36.04, 28.59, 25.69, 25.29, 25.13 ppm.

2.14n: ¹H NMR (400 MHz, C₆D₆): δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 4.85 (s, 2H), 3.47 (s, 3H), 1.03 (s, 12H) ppm; ¹¹B NMR (128 MHz, C₆D₆): δ 22.80 ppm; ¹³C NMR (100 MHz, C₆D₆): δ 145.22, 130.34, 126.89, 83.24, 66.68, 52.06, 25.09 ppm.

2.5 Appendices

2.5.1. Condition Optimization for the Hydroboration of Acetophenone

Table S2.1 Effect of catalyst and HBpin loading on the hydroboration of acetophenone (MeCN).

Reaction scheme for Table S2.1: Acetophenone (2.11a) + HBpin (x equiv.) $\xrightarrow[\text{MeCN (0.2 mL), r.t., 16 h}]{\text{2.10 (y mol\%)}}$ Product 2.12a

Entry	2.10 (mol%)	HBpin (equiv.)	Conversion (%) ^a
1	—	1	3
2	3	1	61
3	5	1	71
4	10	1	90
5	15	1	95
6	10	1.5	97
7	10	2	96

^a Determined by GC with *n*-dodecane as internal standard; based on **2.11a**.

Table S2.2 Effect of catalyst and HBpin loading on the hydroboration of acetophenone (toluene).

Reaction scheme for Table S2.2: Acetophenone (2.11a) + HBpin (x equiv.) $\xrightarrow[\text{toluene (0.2 mL), r.t., 16 h}]{\text{2.10 (y mol\%)}}$ Product 2.12a

Entry	2.10 (mol%)	HBpin (equiv.)	Conversion (%) ^a
1	3	1	63
2	5	1	71
3	10	1	73
4	15	1	88
5	10	1.5	90
6	10	2	91

^a Determined by GC with *n*-dodecane as internal standard; based on **2.11a**.

Table S2.3 Effect of catalyst on the hydroboration of acetophenone (MeCN).

Entry	Catalyst	Loading (mol%)	Conversion (%) ^a
1	—	—	5
2	2.10	10	97
3	FeBr ₂	10	23
4	FeBr ₂	20	23
5	FeBr ₂ •thf ₂	10	20
6	FeBr ₂ •thf ₂	20	11

^a Determined by GC with *n*-dodecane as internal standard; based on **2.11a**.

Table S2.4 Effect of catalyst on the hydroboration of benzaldehyde (MeCN).

Entry	Catalyst (mol%)	Additive (mol%)	Conversion (%) ^a
1	—	—	4
2	2.9 (5)	—	54
3	2.10 (5)	—	>99
4	FeBr ₂ (10)	—	8
5	FeBr ₂ •thf ₂ (10)	—	65
6	2.9 (5)	2.10 (5)	>99
7	2.9 (5)	FeBr ₂ (10)	67
8	2.9 (5)	FeBr ₂ •thf ₂ (10)	>99

^a Determined by GC with *n*-dodecane as internal standard; based on **2.13a**.

2.5.2. Evans NMR Spectrum of 2.10

2.5.3. NMR Spectra of New Organic Compounds

2.12b: ^1H , ^{11}B , ^{13}C

2.12c: ^1H , ^{11}B , ^{13}C

2.12d: ^1H , ^{11}B , ^{13}C , ^{19}F

2.12e: ^1H , ^{11}B , ^{13}C

2.12f: ^1H , ^{11}B , ^{13}C

2.12h: ^1H , ^{11}B , ^{13}C

2.12k: ^1H , ^{11}B , ^{13}C

2.14e: ^1H , ^{11}B , ^{13}C , ^{19}F

2.14e: ^1H , ^{11}B , ^{13}C

2.14f: ^1H , ^{11}B , ^{13}C

2.14n: ^1H , ^{11}B , ^{13}C

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CHAPTER 3:

Amidinato Silylenes as Ligands for Boron-Based Compounds

3.1 Introduction

As is catalysis, the activation of small molecules is not a foreign concept in the domain of transition metal chemistry.^[1] However, the same has rarely been observed for main group compounds before the turn of the millennium. Scientific research was not widely invested in this area with the common consensus, at that time, that main group elements did not possess befitting characteristics for such transformations. Their s or p valence orbitals were assumed to be either fully-occupied or completely empty, and were separated by a large energy gap; in contrast, partially-filled valence d orbitals with relatively similar energies distinguish transition metals from the rest of the periodic table, and is the key to their versatile reactivity.^[2]

In 1981, West and co-workers surmounted these differences through the synthesis of stable disilene (**3.1**, Chart 3.1).^[3] Although it was demonstrated to undergo 1,2-additions and various cycloadditions,^[4] essentially reacting in manners very much akin to its well-studied lighter congener, alkenes, it is remarkable that reaction of the former with organic substrates occurred readily under ambient conditions when transition metal catalysts are generally required for analogies involving the latter. Conceivably, this disparity arises from the inherent weakness of an Si=Si compared to C=C, in which π -bonding is disfavoured for the

heavier atom due to nodal planes present in the 3p orbitals, leading to a poor overlap of electrons as established by the “double bond rule”. This observation is also corroborated by theoretical calculations which indicated a π - π^* gap of ca. 3 eV (vs. 5-6 eV in olefins).^[5]

Chart 3.1 Stable disilene **3.1** and its reactivity.

Interestingly, reactivity of **3.1** with the simplest small molecule, dihydrogen (H_2), or any of its sources, was never reported. It was more than two decades later that the first example of H_2 activation by any main group compound was described. In 2005, Power *et al.* illustrated that heavier alkyne analogue, digermynes **3.2**, reacted with H_2 at room temperature and pressure to afford a series of hydrogenated products, **3.2-H_n** ($n = 2, 3, 4$; Scheme 3.1a).^[6] Theoretical calculations eventually elucidated that cleavage of the H–H bond was promoted by synergistic interactions between its σ and σ^* orbitals with the LUMO($n+$) and HOMO(π) of **3.2** respectively (Scheme 3.1a).^[5] This mechanism resembles that

between H₂ and transition metals (Scheme 3.1b) where, instead of s and p orbitals, partially occupied d orbitals are employed to effect the oxidative addition, and is the first hint that multiply-bonded heavier element compounds can mimic transition metal chemistry.

Scheme 3.1 Mechanism for the activation of H₂ by (a) digermynes **3.2**; and (b) transition metals.

Several other main group species followed to display such fascinating properties (Scheme 3.2).^[7] For example, frustrated Lewis base pair (FLP) systems (**3.3**) pioneered by the group of Stephan was unveiled to react with H₂ reversibly in 2006 (Scheme 3.2a).^[7a] A year later, Bertrand documented that H₂ could be activated by alkyl(amino)carbenes bearing both acyclic (aAAC, **3.4**) and cyclic (cAAC, **3.5** and **3.6**) frameworks (Scheme 3.2b).^[7b] Most notably, treatment of H₂ with Jones' amido-digermynes **3.7**^[7c] and **3.8**^[7d] furnished hydrogenated products, mixed-valence **3.7-H₂** and symmetric **3.8-H₂** respectively, cleanly even under 0 °C in the solid state (Scheme 3.2c). At the same time, acyclic silylenes **3.9**^[7e] and

3.10^[7] featuring significantly obtuse angles at the Si(II) center (109.7(1) and 116.91(5)° respectively) have also flaunted similar abilities (Scheme 3.2d) as forecasted computationally.^[8]

Scheme 3.2 Activation of H₂ by main group compounds: (a) FLP; (b) aAAC and cAACs; (c) amido-digermynes; and (d) acyclic silylenes.

While remarkable, these advances represent only one-half of the way towards catalysis. In a typical catalytic cycle, oxidative addition of a substrate at a metal center, from M^{n+} to $M^{(n+2)+}$, is but the first step (Scheme 3.3a). The resulting, highly-reactive, intermediate then interacts with another substrate in the system (Scheme 3.3b), eventually achieving a *cis* complex (Scheme 3.3c). Normally, this is followed by reductive elimination of the desired product, which concomitantly regenerates the catalytically active species, M^{n+} (Scheme 3.3d). While these processes occur in a sequential manner, all of them are equally critical for effective turnover. In this respect, transition metals remain superior contenders for the task due to their innate ability to adopt various oxidation states.^[9]

Scheme 3.3 Typical catalytic cycle for hydrogenation of olefins.^[10]

Contrastingly, this imperative flexibility is often lacking in s- or p-block elements. In most of the cases mentioned above (Scheme 3.2b-d), thermodynamically favourable addition products are afforded. In consequence,

reversal of this transformation, i.e. cleavage of the stable, newly-formed, E–H (E = main group element) bonds, entails a large barrier difficult to surmount under facile conditions.^[9,11] For instance, the extremely exergonic route from **3.9** to **3.9-H₂** ($\Delta G = -122.2$ kJ/mol) inhibits the backward reaction from **3.9-H₂** to **3.9**.^[7e] Previous theoretical calculations on simplified acyclic and cyclic mono(amino)carbenes conducted by Bertrand and co-workers also indicate that addition of H₂ or NH₃ proceed via eminently exothermic pathways that hamper the reverse experimentally.^[7b]

Nevertheless, reversible binding of small molecules by main group compounds has a handful of precedents.^[12] In 2009, Power and co-workers published groundbreaking work whereby the heavier alkyne analogues, diaryldistannynes **3.11** and **3.12**, react with ethylene easily (Scheme 3.4a).^[12a] Retro-conversion of the formal [2+2] cycloadducts **3.11'** and **3.12'** is possible by heating and/or reducing the pressure of ethylene gas, i.e. under vacuum.^[12a] Similar accomplishments were documented in 2011 by Baceiredo and Kato *et al.* for phosphine-stabilized silylenes **3.13** and **3.14** with olefins to afford the corresponding pentacoordinate siliranes **3.13'** and **3.14'** (Scheme 3.4b).^[12b,c] 2014 even saw the remarkable bulky tin(II) (**3.15**) and germanium(II) (**3.16**) hydrides generating turnover frequencies that rival their transition metal counterparts when employed as catalysts in the hydroboration of carbonyls (Scheme 3.4c).^[12d] More recently, Inoue described an iminosilylene (**3.17**) that readily undergoes intramolecular C=C bond insertion to give the isolable silepin **3.17'** (Scheme 3.4d).^[12e] Upon heating **3.17'**, **3.17** can be detected by UV/Vis spectroscopy; otherwise, **3.17'** acts as a “masked” silylene for further reaction with a range of Lewis acids and small molecules.^[12e]

Scheme 3.4 Selected examples of reversible small molecule activation by low valent group 14 element compounds; TOF = turnover frequency.

The above results collectively suggest that low valent main group compounds have the propensity to parallel transition metal chemistry and offer themselves as promising substitutes in arenas previously exclusive to the former. One such field that branches into the interests of our research is the stabilization of otherwise vastly reactive main group species. Several precedents regarding silylenes surfaced in literature around 2012, whereby silylene fluorides and silylene

hydrides, not known to be stable independently, were isolated via coordination to transition metal fragments (Chart 3.2).^[13]

Chart 3.2 Transition metal-stabilized (a) silylene fluoride; and (b) silylene hydrides.

Complementary findings are likewise available for group 13 elements; particularly, transition metal borylene complexes have been deeply investigated.^[14] While free borylenes [LB:] (L = supporting ligand) remain elusive even up till today, its high reactivity can be adequately sequestered in the coordination sphere of a transition metal as early as 1998.^[15] Compounds of type **3.18** to **3.20** (Chart 3.3) are but a few examples amongst the plethora of such adducts that now exists. Lately, however, similar advancements have been accomplished “metal-free” by utilizing spectacular main group compounds.^[16] Upon closer scrutiny, one would discern the latent similarities between main group “stabilizing agents” and their transition metal predecessors. As depicted in Chart 3.3, the structure of heteroallene **3.21**^[16a] holds considerable resemblance to terminal borylenes (type **3.18**). Borylenes **3.22**^[16b] and **3.23**^[16c] starring identical donor carbenes are also reminiscent of homodinuclear bridging borylenes (type **3.19**). Furthermore, unsymmetrical analogues (**3.24** and **3.25**) described in 2014^[16d] seem to mimic

heteronuclear bridging borylenes (type **3.13**). One unanimous conclusion can be drawn from these evidences, which is that low valent main group species can indeed demonstrate “transition metal-like” chemistry.

Chart 3.3 Selected (a) transition metal-; and (b) main group-borylene complexes.

Consequently, we were prompted to investigate if such possibilities can be developed with silylenes. Riding on our recent successes (Chart 3.4)^[17] in isolating the first *N*-heterocyclic silylene (NHSi)-stabilized digermanium(0) complex **3.26**^[17a] and synthetically-challenging heterobinuclear Si(II)→E(II) adducts of group 14 elements in the +2 oxidation state (**3.27** to **3.29**),^[17b] we chose to extend this work to group 13 elements.

Chart 3.4 NHSi-stabilized main group species described by our group.

As early as 1998, the β -diketiminato aluminium cation **3.30** was found to react with ethylene, which can be removed upon treatment of *N,N'*-dimethylaniline (Scheme 3.5a).^[18a] Truly reversible [4+2] cycloadditions have lately been identified between ambiphilic 1,3,2,4-diazadiborinane **3.31** and ethylene, styrene derivatives,^[18b] and even CO_2 ^[18c] (Scheme 3.5b). However, in terms of intramolecular examples proficient in performing reversible hydrogenation, the literature is still seemingly limited to that of Stephan's frustrated Lewis base pairs that operate by the mutual efforts of well-separated phosphine and borane components (**3.3**, Scheme 3.2a).^[7a] In 2017, the group of Driess came very close with an intramolecular silylene-borane (**3.32**) which adds to H_2 and dehydrogenates water, albeit in separate and irreversible transformations (Scheme 3.5c).^[18d]

Scheme 3.5 Selected examples of reversible small molecule activation by group 13 element-containing compounds.

These results suggest that silylene boranes have the potential to bind, as well as eliminate H₂ and encouraged us to determine if, in particular, silylene-borane adducts harbored analogous characteristics. In this chapter, we report a straightforward synthetic approach towards a series of boronium cations supported by readily accessible amidinato silicon(II) derivatives [L(R)Si:] (L = PhC(N*t*Bu)₂; **3.33**: R = N(SiMe₃)₂, **3.34**: NMe₂, **3.35**: Cl).^[19-21] In selected instances,

intramolecular C(sp³)–H bond activation was observed to afford endocyclic boronium cations. The subsequent reactivities of these species were probed with H₂ and its source, ammonia-borane [NH₃•BH₃], and proved to regenerate a precursor. Characterization of all new compounds are detailed in the following section.

3.2 Results and Discussion

3.2.1. Synthesis of Amidinato Silylene-Borane Adducts

Treatment of amidinato silicon(II) amide **3.33**^[19] with a slight excess of borane-tetrahydrofuran complex [BH₃•THF] in toluene afforded the silylene-borane adduct [L{(SiMe₃)₂N}Si:→BH₃] (**3.36**, Scheme 3.6) overnight. The air- and moisture-sensitive colourless crystalline solids were isolated in 79% yield. It should be noted that while a vacant p orbital exists on the low valent silicon center, creating a π -system next to the boron, **3.36** does not undergo self-hydroboration as with most π -complexes of boranes.^[22] The silylene species simply acts as a Lewis base to donate its lone pair electrons into the empty p orbital of boron. As in *N*-heterocyclic carbene (NHC)-boranes, this can be ascribed to poor π -acceptor ability of **3.33** formerly estimated by calculations.^[23]

Scheme 3.6 Synthesis of silylene-borane **3.36**.

X-ray quality crystals of **3.36** were obtained from a saturated toluene solution at ambient temperature; its structure was unequivocally established by single crystal XRD (Figure 3.1). Of the two independent molecules present in the asymmetric unit, only one will be discussed for clarity. Both Si1 and B1 atoms adopt distorted tetrahedral geometries. The amidinate bite angle around Si1 is 71.17(8)°, only moderately enlarged from its precursor (69.09(4)°).^[19] While the Si–N(amidinate) bond lengths (1.8402(17) and 1.8396(17) Å) in **3.36** are compressed

compared to **3.33** (1.8776(10), 1.8780(10) Å), they are still longer than Si–N single bonds, for example Si–N(SiMe₃)₂ in **3.33** (1.769(7) Å) and **3.36** (1.7258(17) Å).^[19] Overall, the structural parameters of the silylene unit remain relatively unchanged transitioning from **3.33** to **3.36**, suggesting that silylene-character is preserved in the latter. The Si–B bond featured in **3.36** measures 1.974(3) Å and is comparable with previously known adducts including hydridosilylene-borane^[24] and *N*-heterocyclic carbene (NHC)-stabilized silicon dichloride-borane^[25] (Chart 3.5).

Figure 3.1 ORTEP drawing of **3.36** with thermal ellipsoids at the 30% probability level. As there are two independent molecules in the asymmetric unit with slightly different bond lengths and angles, only one independent molecule is discussed here for clarity. For the same reason, selected hydrogen atoms are elided. Selected bond lengths (Å) and bond angles (°): Si1–B1 1.974(3), B1–H1B 1.11(2), B1–H2B 1.11(3), B1–H3B 1.12(2), Si1–N1 1.8402(17), Si1–N2 1.8396(17), Si1–N3 1.7258(17); Si1–B1–H1B 101(1), Si1–B1–H2B 114(1), Si1–B1–H3B 107(1), N1–Si1–N2 71.12(8), N1–Si1–N3 111.81(8), N3–Si1–B1 126.1(1).

Chart 3.5 Structures, Si-B bond lengths (Å), ^{11}B NMR signals (ppm) and coupling constants (Hz) of previously reported silylene-boranes.

Compound **3.36** was similarly characterized by multinuclear NMR spectroscopy. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra exhibit a set of signals attributable to the amidinate and $\text{N}(\text{SiMe}_3)_2$ ligands. In its ^{11}B NMR spectrum, a 1:3:3:1 quartet is detected at δ -38.17 ppm with a coupling constant of 91.3 Hz, corresponding to the BH_3 moiety. While the former is slightly downfield shifted, the latter is reminiscent of related examples (Chart 3.5).^[24,25] Two sharp signals (δ 4.54 and 9.08 ppm) owing to the SiMe_3 groups could be identified in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum, along with an inverse-phased, weakly-resonating, quartet (δ 22.05 ppm, $^1J_{\text{Si-B}} = 67.1$ Hz) for the silylene Si. The absence of B-H signals in ^1H NMR spectroscopy can be rationalized by the virtue of extensive line-broadening compelled by the adjacent quadrupolar boron. This phenomenon was also observed prior by Robinson *et al.* and other research groups.^[22,26]

In an analogous reaction with another amidinato silicon(II) amide, **3.34**,^[20] the corresponding Lewis base adduct $[\text{L}(\text{Me}_2\text{N})\text{Si}:\rightarrow\text{BH}_3]$ (**3.37**, Scheme 3.7) could be formed. However, the ^1H NMR spectrum of the isolated crystalline solids revealed two sets of signals for the ligand backbones in a ratio of ca. 1:5, neither of which were attributable to the precursor. As such, it is speculated that in the presence of excess borane, a second coordination occurs by the donation of the amido lone pair electrons to give **3.37'** (Scheme 3.7). Indeed, when equimolar

borane was employed instead, **3.37** could be cleanly generated. This contrasts the reaction of **3.33** with excess borane, whereby **3.37** is yielded as the sole product. Conceivably, the steric shielding provided by the “helmet-like” SiMe₃ groups prohibits or significantly impedes the addition of a second borane to the amido moiety.^[19]

Scheme 3.7 Synthesis of silylene-borane **3.37**.

From a pure sample of **3.37**, colourless crystals were grown from toluene at ambient temperature; they were analysed by XRD to confirm the structure as illustrated in Figure 3.2. The Si1–B1 bond length in this case is 1.961(4) Å; the geometries around Si1 and B1 are both distorted tetrahedral. In general, the structural parameters of **3.37** are evocative of **3.36** and in line with other known silylene boranes.^[24,25] It should be noted that **3.37** can be isolated in a relatively high yield of 73%, though the crystals are air- and moisture-sensitive.

Multinuclear NMR spectroscopy was performed on **3.37** to achieve an all-rounded characterization. The ligand backbones were well-observed in both the ¹H and ¹³C{¹H} NMR spectra; its ¹¹B NMR signal resides at δ -46.89 ppm (q, ¹J_{B–H} =

91.1 Hz), which coincides excellently with pertinent precedents (Chart 3.5); the silylene resonance in $^{29}\text{Si}\{^1\text{H}\}$ NMR is located as a broad hump at δ 30.24 ppm.

Figure 3.2 ORTEP drawing of **3.37** with thermal ellipsoids at the 30% probability level. Selected hydrogen atoms are elided for clarity. Selected bond lengths (Å) and bond angles (°): Si1-B1 1.961(4), B1-H1B1 1.12(2), B1-H2B1 1.11(3), B1-H3B1 1.11(3), Si1-N1 1.832(2), Si1-N2 1.839(2), Si1-N3 1.686(2); Si1-B1-H1B1 107(1), Si1-B1-H2B1 109(1), Si1-B1-H3B1 110(1), N1-Si1-N2 70.80(9), N1-C5-N2 105.8(2), N1-Si1-N3 109.7(1), N2-Si1-B1 118.4(1), N3-Si1-B1 120.5(1).

Scheme 3.8 Synthesis of silylene-borane **3.38**.

To complete this series, we reproduced the results of Roesky and co-workers for the synthesis of silylene-borane adduct $[\text{L}(\text{Cl})\text{Si}:\rightarrow\text{BH}_3]$ (**3.38**, Scheme 3.8).^[24] By following their outlined procedure, the target compound was obtained upon treatment of monochlorosilylene **3.35**^[21] with equimolar $\text{BH}_3\cdot\text{THF}$. While the ^1H and ^{11}B NMR spectra acquired were consistent with documented values, we

were interested in the structural parameters of **3.38** which were not previously reported.

On that account, we harvested single crystals of **3.38** from a saturated toluene solution and examined them by XRD. Figure 3.3 shows a solid state structure agreeing with the formation of adduct **3.38**. The Si–B distance of 1.893(15) Å hovers at the short edge of the usual range; the Si–Cl length (2.049(3) Å) is reduced by ca. 0.1 Å from that in its precursor (2.156(1) Å), as are the Si–N(amidinate) bonds (1.799(2), 1.796(2) Å) in comparison to 2.25 (1.870(2), 1.917(2) Å).^[21] It should be noted that BH₃ and Cl are disordered in the asymmetric unit.

Figure 3.3 ORTEP drawing of **3.38** with thermal ellipsoids at the 30% probability level. Selected hydrogen atoms are elided for clarity. Selected bond lengths (Å) and bond angles (°): Si1–B1 1.893(15), B1–H1A 1.15, B1–H1B 1.17, B1–H1C 1.17, Si1–N1 1.799(2), Si1–N2 1.796(2), Si1–Cl1 2.049(3); Si1–B1–H1A 109, Si1–B1–H1B 109, Si1–B1–H1C 106, N1–Si1–N2 72.87(9), N1–C5–N2 105.9(2), N2–Si1–Cl1 112.2(1), Cl1–Si1–B1 118.9(6), B1–Si1–N1 118.8(6).

3.2.2. Synthesis of Amidinato Silylene-Monotriflate Boranes

With several stable silylene-boranes in hand, we envisioned various hydride substitution reactions. While cyano groups are enormously attractive due to their ability to introduce B–H umpolung,^[27,28] i.e. induce protic character on H, polytriflate derivatives with multiple excellent leaving groups are also desirable targets. In the case of the former, however, more than a single cyano group is likely required in order to compensate for the weakly π -accepting silylene ligand.^[27] Furthermore, selective displacement of only one of the alike substituents is typically not viable. Considering that sterics have also proven to hamper the reactivity of ditriflate species,^[29] we tackled the synthesis of mono-substituted silylene-boranes.

Scheme 3.9 Synthesis of silylene-monotriflate borane **3.39**.

Treatment of **3.36** with equimolar methyl triflate [MeOTf] (OTf = OSO₂CF₃) furnished [L{(SiMe₃)₂N}Si:→BH₂OTf] (**3.39**, Scheme 3.9) as the sole product in 92% yield. Air- and moisture-sensitive colourless crystals could be obtained from a saturated toluene solution and were analyzed by XRD (Figure 3.4). The Si1–B1 bond length in **3.39** (2.011(6) Å) is stretched with respect to its precursor (1.974(3) Å), an observation consistent with the conversion of Bertrand's [cAAC:→BH₃] (C–B: 1.517(4) Å) to [cAAC:→BH₂OTf] (C–B: 1.601(1) Å).^[29] Perhaps, this is also a consequence of steric constraints arising from the covalently-attached OTf group, in which the B–O bond length of 1.563(7) Å corresponds to a single bond.

Figure 3.4 ORTEP drawing of **3.39** with thermal ellipsoids at the 10% probability level. Selected hydrogen atoms are elided for clarity. Selected bond lengths (Å) and bond angles (°): Si1-B1 2.011(6), B1-H1A 1.01(4), B1-H1B 1.02(3), B1-O1 1.563(7), Si1-N1 1.821(3), Si1-N2 1.815(3), Si1-N3 1.711(3); Si1-B1-H1A 114(3), Si1-B1-H1B 114(2), Si1-B1-O1 104.1(3), O1-B1-H1A 112(3), B1-Si1-N1 109.7(2), B1-Si1-N2 110.1(2), B1-Si1-N3 122.0(2), N1-Si1-N3 116.4(1).

While the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **3.39** are expected and uninteresting, the downfield-shifted ^{11}B NMR signal (δ -9.76 ppm) broadens and coupling with adjacent H atoms is no longer well-defined. At the same time, the B–Si resonance was tricky to identify in $^{29}\text{Si}\{^1\text{H}\}$ NMR. Previous accounts associate this with quadrupolar effects; the occurrence is more pronounced with unsymmetrically-distributed charges around the boron and complexes with higher molecular weights.^[22] In the ^{19}F NMR spectroscopy, a sharp singlet at δ -74.50 ppm verifies the non-ionized triflate unit.

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Figure 3.5 ORTEP drawing of **3.40** with thermal ellipsoids at the 30% probability level. As there are two independent molecules in the asymmetric unit with slightly different bond lengths and angles, only one independent molecule is discussed here for clarity. For the same reason, selected hydrogen atoms are elided. Selected bond lengths (Å) and bond angles (°): Si1-B1 2.005(5), B1-H1B1 1.13(3), B1-H1B2 1.13(3), B1-O1 1.578(5), Si1-N1 1.822(3), Si1-N2 1.822(3), Si1-N3 1.686(3); Si1-B1-H1B1 107(2), Si1-B1-H1B2 107(2), Si1-B1-O1 114.2(3), H1B1-B1-O1 111(2), N1-Si1-N2 72.0(1), N1-C5-N2 105.7(3), N1-Si1-N3 109.5(1), B1-Si1-N2 119.3(2), B1-Si1-N3 114.9(2).

3.2.3. Synthesis of Amidinato Silylene-Boronium Cations

Upon successful installation of a favourable leaving group, we endeavoured to displace it by the addition of a Lewis base into the respective monotriflate systems. Contrary to our anticipation, no palpable reaction was observed between **3.39** and silylenes **3.34** or **3.35** under ambient conditions. Nevertheless, we were pleased to achieve the desired boronium salts upon heating the mixture in refluxing toluene (Scheme 3.11).

Scheme 3.11 Synthesis of bis(silylene)-boronium salts **3.42** and **3.43**.

The structures of **3.42** and **3.43** are as exemplified in Figures 3.6 and 3.7 respectively. In both instances, all boron and silylene silicon atoms assume highly distorted tetrahedral geometries. The Si(silylene)–B–Si(silylene) angle in **3.42** is 138.6(1)°, whereas that in **3.43** is only 130.5(3)°. The substantial widening can be justified by the *syn* configuration of the R groups (N(SiMe₃)₂ and NMe₂) supporting the silylenes, resulting in excess steric congestion around the B atom in **3.42**. This

situation is eased in the case of **3.43**; the R groups (N(SiMe₃)₂ and Cl) of the silylenes adopt the opposite *anti* mode and thus reduce the angle around B1.

Most meaningfully, XRD studies clearly revealed both yielded compounds as charge-separated species. The nearest B...O distance is 10.654(9) Å and 8.391(9) Å in **3.42** and **3.43** respectively, momentarily exceeding the sum of their van der Waal's radii (ca. 3.48 Å). The ¹⁹F NMR spectra exhibiting singlets at δ -77.17 and -80.72 ppm are in agreement with free triflate anions; the ¹¹B NMR signals now resolve into sharp triplets at δ -45.93 (¹J_{B-H} = 81.4 Hz) and -44.86 (¹J_{B-H} = 84.9 Hz) ppm. The concomitant shift into an upfield region is common for four-coordinate boronium cations. Still, neither **3.42** nor **3.43** displayed discernible resonances attributable to B-H and B-Si.

Figure 3.6 ORTEP drawing of **3.42** with thermal ellipsoids at the 30% probability level. Selected hydrogen atoms are elided for clarity. Selected bond lengths (Å) and bond angles (°): Si1-B1 1.973(2), Si2-B1 1.984(2), Si1-N1 1.846(2), Si1-N2 1.839(2), Si1-N3 1.691(2), Si2-N4 1.841(2), Si2-N5 1.833(2), Si2-N6 1.718(2); Si2-B1-Si1 138.6(1), H2BB-B1-H1BB 103(2), Si2-B1-H2BB 101(1), Si1-B1-H1BB 101(1), N1-Si1-N2 71.20(9), N1-Si1-N3 108.9(1), B1-Si1-N2 110.6(1), N4-Si2-N5 71.45(8), N4-Si2-N6 106.2(2), N4-Si2-N6 115.33(9), B1-Si2-N5 105.1(1).

Figure 3.7 ORTEP drawing of **3.43** with thermal ellipsoids at the 20% probability level. Selected hydrogen atoms and solvent molecules are elided for clarity. Selected bond lengths (Å) and bond angles (°): Si1-B1 1.972(6), Si4-B1 1.957(6), Si1-N1 1.829(4), Si1-N2 1.821(4), Si1-N3 1.715(4), Si4-N4 1.805(4), Si4-N5 1.819(4), Si4-Cl1 2.063(2); Si4-B1-Si1 130.5(3), Si1-B1-H1B1 97.4, H1B1-B1-H1B 128.6, H1B-B1-Si4 102, N2-Si1-N1 71.5(2), N1-Si1-N3 115.3(2), N3-Si1-B1 114.9(2), B1-Si1-N2 121.7(2), N5-Si4-N4 72.9(2), N4-Si4-B1 112.2(2), B1-Si4-Cl1 122.3(2), Cl1-Si4-N5 107.6(1).

Scheme 3.12 Synthesis of bis(silylene)-boronium salts **3.42** and **3.44**.

Bis(silylene)-boronium salt **3.42** can be obtained via an alternative synthetic route between **3.40** and **3.33** (Scheme 3.12), albeit with only minor improvements to the yield. Further exploration of the reactivity of **3.40** with **3.34** afforded the symmetric cation-containing species **3.44** in approximately 90% isolated yield. While single crystals suitable for XRD studies could not be readily accessed, its structure is proposed on the basis of multinuclear NMR spectroscopy. Singlets at δ 1.23 and 2.81 ppm in the ^1H NMR spectrum with an integral ratio of 36:12 correspond to the *t*Bu and NMe₂ substituents respectively, suggesting that both silylene ligands are chemically-equivalent on an NMR timescale. A triplet is observed at δ -51.95 ($^1J_{\text{B-H}} = 84.4$ Hz) ppm in the ^1H -coupled ^{11}B NMR; it is shifted from its precursor and indicative of a four-coordinate boronium environment with two adjacent H atoms. Additionally, the ^{19}F NMR spectroscopy corroborates an ionized triflate moiety with a characteristic resonance at δ -78.99 ppm.

Likewise to **3.42**, bis(silylene)-boronium salt **3.43** can be envisaged from monotriflate borane **3.41** and Lewis base **3.33** (Scheme 3.13). Multinuclear NMR spectroscopy affirmed that the colourless crystalline solids collected upon work-up are exact in identity to **3.43**.

Scheme 3.13 Alternative synthesis of bis(silylene)-boronium salt **3.43**.

The reactivity of principal monotriflate-borane **3.39** was then investigated with a more traditional Lewis base, 4-dimethylaminopyridine (DMAP). The formation of analogous boronium salt **3.45** (Scheme 3.14) demonstrates that our protocol is not limited to silylenes and can be effective with compounds bearing variant donor atoms as well.

Scheme 3.14 Synthesis of silylene-boronium salt **3.45**.

The crystal structure of **3.45** (Figure 3.8) shows an acute ligand–B1–ligand angle of 113.3(4)°, in which the tetrahedral geometry around B1 deviates only marginally from ideal. In contrast to the crowded situation in aforementioned **3.42**

and **3.43**, the less sterically-demanding DMAP ligand allows for less distortion. The B $\cdots$ O interactions average to 7.43 Å in this case.

With regards to its NMR, the ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra appeared commonplace. While the free triflate unit resonates in the expected region at δ - 77.36 ppm in ^{19}F NMR, the ^{11}B signal at δ -15.74 ppm is broad with no obvious coupling patterns to the adjacent H atoms. Moreover, it is only slightly upfield shifted compared to precursor **3.39** (δ -9.76 ppm). One possible reason for these is an increased electronic field gradient^[22] induced by DMAP on the boron center. The non-conforming behavior further highlights the inherently differing natures between conventional donors and their silylene analogues.

Figure 3.8 ORTEP drawing of **3.45** with thermal ellipsoids at the 30% probability level. Selected hydrogen atoms are elided for clarity. Selected bond lengths (Å) and bond angles ($^\circ$): Si1-B1 2.043(7), B1-H1BB 1.10(5), B1-H2BB 1.11(4), B1-N4 1.559(9), Si1-N1 1.829(4), Si1-N2 1.831(4), Si1-N3 1.710(3); Si1-B1-N4 113.3(4), Si1-B1-H1BB 102(2), Si1-B1-H2BB 104(2), N1-Si1-N2 71.7(2), N1-Si1-N3 115.4(2), N3-Si1-H1BB 121(1).

3.2.4. Synthesis of Endocyclic Boronium Cations via C(sp³)-H Activation and H₂ Elimination

Thus far, while refluxing monotriflate borane **3.39** with Lewis bases all led to the displacement of triflate by Lewis base, attempting the same reaction with slightly bulkier amidinato amidosilylene **3.33** did not proceed as expected. Upon refluxing a mixture of **3.39** and **3.33** in toluene overnight, the reaction was filtered hot. Slow evaporation of the solvent, or gradual cooling to room temperature, afforded block-like colourless crystals. Subsequent XRD analysis established the structure of the product to be that of endocyclic boronium salt **3.46** (Scheme 3.15, Figure 3.9), rather than the anticipated bis(silylene)-boronium salt **3.46'**.

Scheme 3.15 Synthesis of endocyclic boronium salt **3.46/3.46-d**.

The formation of **3.46** is postulated to occur via the borylation of C(sp³)-H of one of the six terminal methyl groups emanating from the N(SiMe₃)₂ ligand. Such metal-free electrophilic aliphatic borylation is rare as it necessitates for the boron center to bear a sufficiently Lewis acidic empty p orbital, while simultaneously

possessing an orthogonal filled orbital. Only two examples have been reported to date (Scheme 3.16).^[30] In the first instance, upon hydride abstraction from **3.47** by strong electrophile $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$, the borenium intermediate **3.47A** undergoes intramolecular C–H borylation with concomitant loss of H_2 to form the final product **3.47'**.^[30a] More recently, Prokofjevs communicated that **3.48**, upon thermally-induced H_2 loss, affords borenium cation **3.48A**, which underwent intramolecular C–H borylation by B–B bond cleavage.^[30b]

Scheme 3.16 Reported cases of metal-free electrophilic aliphatic borylation.

We propose that the presence of Lewis base in solution induces the dissociation of OTf, leaving a vacant p orbital on the boron center (**3.46A**, Scheme 3.17). Less sterically-hindered Lewis bases are able to quickly coordinate to the boron atom, forming acyclic boronium salts, as demonstrated in section 3.4.3. In this case, however, the σ -bond metathesis reaction between $\text{C}(\text{SiMe}_3)\text{--H}$ and B--H is faster than the coordination of **3.33** to **3.46A**, affording **3.46** and H_2 (Scheme 3.17). The slow coordination of **3.33** can be attributed to its weak Lewis basicity, in addition to its bulky nature. Nevertheless, this coordination should be faster than a second metathesis reaction, as the double-borylated derivative (**3.46C**, Scheme

3.17) was not observed experimentally. This mechanism was also validated by deuterium-labelling studies, which gave **3.46-d** as the borylated product.

Scheme 3.17 Proposed mechanism for the formation of **3.46**.

Crystals of **3.46** were isolated in 51% yield. The solid state structure of its cation is illustrated in Figure 3.9. It features rather similar Si–B bond lengths (2.028(4), 2.042(4) Å) which are elongated compared to its precursor (2.011(6) Å) and closely-related analogues **3.42** (1.973(2), 1.984(2) Å) and **3.43** (1.972(6), 1.957(6) Å). The B1–C20 of 1.654(6) Å is significantly stretched with respect to typical B–C single bonds (1.59 Å). However, it has been observed previously by Kinjo *et al.* in the ethylene adduct of 1,3,2,4-diazadiborinine **3.31** (1.653(5), 1.671(5) Å; Scheme 3.5b). The B⋯O interaction (8.43(1) Å), as per other boronium salts synthesized thus far, greatly exceeds the covalent radii. The Si(silylene)–B–Si(silylene) angle in this case (137.8(2)°) largely resembles that in **3.42** (138.6(1)°) and is evidence of the sterically-crowded situation around the distorted tetrahedral boron atom prompted by the two bulky amidosilylene moieties.

The ¹¹B NMR reveals a doublet at δ -33.01 (¹J_{B–H} = 77.7 Hz) ppm, corresponding to the central boronium atom. The ¹⁹F NMR signal of δ -78.80 ppm

is in accordance to the ionized triflate group. Only SiMe_n resonances could be identified in the $^{29}\text{Si}\{^1\text{H}\}$ NMR, presumably due to quadrupolar broadening of the B–Si signals.

Figure 3.9 ORTEP drawing of **3.46** with thermal ellipsoids at the 30% probability level. Selected hydrogen atoms, disordered triflate counter anion and solvent molecules are elided for clarity. Selected bond lengths (Å) and bond angles (°): B1–H1B 1.275, B1–Si1 2.028(4), B1–Si4 2.042(4), B1–C20 1.654(6); Si1–B1–Si4 137.8(2), Si4–B1–H1B 98.9, H1B–B1–C20 114.7, C20–B1–Si1 100.9(3), B1–Si1–N3 102.5(1), Si1–N3–Si3 113.8(1), N3–Si3–C20 98.3(2), Si3–C20–B1 111.6(3).

Similar C–H borylations were observed when **3.39** was treated separately with new amidinato amidosilylene $[\text{L}(\text{L}')\text{Si}:]$ (**3.49**, Scheme 3.18; $\text{L}' = \text{N}(\text{tBu})\{\text{C}(\text{Ph})=\text{NtBu}\}$) and previously reported IPr carbene $[(\text{HCNAr})_2\text{C}:]^{[31]}$ (**3.51**, Scheme 3.18; $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$). **3.49** (Figure 3.10) can be simply prepared by treating $[\text{L}(\text{Cl})\text{Si}:]$ (**3.35**) with equimolar amidinate-lithium salt $[\text{LLi}]$ (see section 0 for detailed experimental procedure).

Scheme 3.18 Synthesis of endocyclic boronium salts **3.50** and **3.52**.

In both instances H_2 was likewise eliminated, generating endocyclic boronium salts **3.50** (Figure 3.11) and **3.52** (Figure 3.11) respectively (Scheme 3.18). Their ligand-B-ligand angles are wide (**3.50**: $138.0(3)^\circ$; **3.52**: $135.9(2)^\circ$), with B–C(endocyclic) bond lengths (**3.50**: $1.650(9) \text{ \AA}$; **3.52**: $1.633(5) \text{ \AA}$) reminiscent of **3.46**. In contrast, the B–C(carbene) bond length in **3.52** is $1.607(4) \text{ \AA}$ and more akin to the B–C single bond.

Crystals of **3.50** can be isolated cleanly in moderate yields (66%). Conversely, those of **3.52** are tricky to separate from side product $[\mathbf{3.51} \cdot \text{HOTf}]$ due to extremely similar solubilities, leading to a complicated mixture of signals in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. However, ^{11}B NMR undoubtedly indicates the formation of both boronium salts with doublets at $\delta -38.66$ ($^1J_{\text{B-H}} = 81.4 \text{ Hz}$) ppm (**3.50**) and $\delta -28.59$ ($^1J_{\text{B-H}} = 78.3 \text{ Hz}$) ppm (**3.52**).

Figure 3.10 ORTEP drawing of **3.49** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are elided for clarity. Selected bond lengths (Å) and bond angles (°): Si1-N1 1.883(1), Si1-N2 1.874(1), Si1-N3 1.794(1), C5-N1 1.347(2), C5-N2 1.341(2), C20-N3 1.421(2), C20-N4 1.274(2); N1-Si1-N2 69.43(6), N2-Si1-N3 107.04(6), N3-Si1-N1 105.45(6), N1-C5-N2 105.5(1), N3-C20-N4 119.4(1).

Figure 3.11 ORTEP drawing of **3.50** with thermal ellipsoids at the 30% probability level. Selected hydrogen atoms and solvent molecules are elided for clarity. Selected bond lengths (Å) and bond angles (°): B1-H1B 1.22(5), B1-Si1 2.018(6), B-Si4 2.023(7), B1-C21 1.650(9); Si1-B1-Si4 138.0(3), Si4-B1-H1B 103(3), H1B-B1-C21 111(3), C21-B1-Si1 100.1(4), B1-Si1-N3 104.1(2), Si1-N3-Si3 110.1(2), N3-Si3-C21 101.9(2), Si3-C21-B1 107.8(4).

Figure 3.12 ORTEP drawing of **3.52** with thermal ellipsoids at the 30% probability level. Selected hydrogen atoms and solvent molecules are elided for clarity. Selected bond lengths (Å) and bond angles (°): B1-H1B 1.15(3), B1-Si1 2.014(3), B1-C22 1.607(4), B1-C16 1.633(5); Si1-B1-C22 135.9(2), C22-B1-H1B 103(2), H1B-B1-C16 108(2), C16-B1-Si1 100.9(2), B1-Si1-N3 100.9(1), Si1-N3-Si2 110.5(1), N3-Si2-C16 102.5(1), Si2-C16-B1 105.1(2).

3.2.5. Reactivity of Endocyclic Boronium Cations with Molecular H₂ and Ammonia-Borane

The mechanism of sigma bond metathesis between C(SiMe₃)–H and B–H resembles that of transition metal-like oxidation addition, and aroused our interest to investigate whether reversible aliphatic C–H borylation is possible. Furthermore, with the precedent of H₂ fixation and elimination by intramolecular silylene-borane FLP **3.32** (Scheme 3.5c), we were intrigued to examine similar capabilities with our endocyclic boronium salts. Since C–H borylation occurred under refluxing conditions, we anticipate that the reverse reaction can be achieved at room temperature. Hence, compounds **3.46**, **3.50** and **3.52** were separately exposed to an atmosphere of H₂ (1 atm). In toluene-*d*₈ at room temperature, no reaction was detected, presumably due to sparing solubility of the boronium salts in hydrocarbons. Swapping the solvent for THF-*d*₈ allowed for reaction between **3.46** and H₂ to be observed by ¹¹B NMR spectroscopy after ca. 12 hours (Figure 3.13).

Figure 3.13 Reaction of **3.46** and H₂ as monitored by ¹¹B NMR spectroscopy; flat baseline obtained by utilizing a quartz NMR tube during data acquisition.

The quartet signal produced around δ -38 ppm was identified to be silylene-borane precursor **3.36** (Scheme 3.19). The rate of reaction is slow and the reaction cannot be completed in 48 h. Besides the formation of **3.36**, a mixture of unidentified by-products was observed in THF- d_8 . They could comprise an OTf anion as indicated by ^{19}F NMR spectroscopy. To further understand the mechanism of the reaction, ammonia-borane $[\text{NH}_3\cdot\text{BH}_3]$ was selected as a H_2 source to stoichiometrically react with **3.46**. Upon stirring in toluene for 6 hours at room temperature, a cloudy solution was formed. From the filtrate, colourless crystals, verified to be **3.36**, were obtained. The residue, extracted with THF, were confirmed to be $[\text{L}\{(\text{SiMe}_3)_2\text{N}\}\text{Si}(\text{H})]\text{OTf}$ (**3.53**, Scheme 3.19) by ^1H and ^{19}F NMR spectroscopy.

Scheme 3.19 Reactivity of **3.46** with $\text{NH}_3\cdot\text{BH}_3$.

On the basis of this experimental results, we propose the mechanism for the reaction of **3.46** and H_2 (Scheme 3.20). $[\text{L}\{\text{N}(\text{SiMe}_3)_2\}\text{Si}:]$ (**3.33**) in compound **3.46** appears to dissociate in solution to form borenium intermediate **3.46B**, whereby a dihydrogen molecule inserts into the B–C bond to form compound **3.39**. It further undergoes a frustrated Lewis pair pathway to react with H_2 and **3.33** to form isolated products **3.36** and **3.53**. There is a possibility that **3.53** could further react

with H₂ to form triflate-anion-containing compounds, which cannot be identified as yet.

Scheme 3.20 Proposed mechanism for the reaction of **3.46** and H₂.

It should be noted that with endocyclic boronium salt **3.50**, no observable reaction with H₂ took place under ambient conditions and heating only generated an intractable mixture. Carbene-stabilized analogue **3.52** was similarly found to be inert towards H₂, even up to 120 °C and after 3 days, plausibly due to the overly strong σ -donating properties of the NHC ligand.

3.3 Conclusion

A straightforward synthetic route to access a series of acyclic silylene-boronium salts was developed. Reaction of silylene with borane followed by treatment with MeOTf and subsequent refluxing with Lewis base provided the title compounds **3.42** to **3.45**.

The first reversible amidinato silylene-directed aliphatic C-H borylation was also reported. The reaction of the amidinato silylene monotriflate complex **3.39** undergoes an intramolecular aliphatic C-H borylation with the amidinato amidosilylene **3.33** in refluxing toluene to form the endocyclic amidinato silylene-boronium cation **3.46**. It can react with hydrogen gas to regenerate the amidinato silylene-borane complex **3.36**.

3.4 Experimental

General considerations: All manipulations, unless otherwise stated, were carried out by using standard Schlenk and glovebox techniques under an atmosphere of high purity argon. Toluene and hexane were dried and distilled over molten potassium or dried using a MBraun Solvent Purification System. Benzene- d_6 , THF and THF- d_8 were dried and distilled over molten potassium. CD_2Cl_2 was dried and distilled over calcium hydride. All NMR spectra were recorded on Bruker Avance 400 or Jeol ECA 400 MHz spectrometers. 1H NMR spectra were referenced to residual solvent peaks. All chemicals were used as received, unless stated otherwise. **3.33**,^[19] **3.34**,^[20] **3.35**^[21b] and **3.38**^[24] were synthesized according to literature procedures.

X-ray data collection and structural refinement: Intensity data for compounds **3.36** to **3.40**, **3.42**, **3.43**, **3.45**, **3.46**, **3.49**, **3.50** and **3.52** were collected by using a Bruker APEX II diffractometer. Reflections were measured at T / K (see section 3.5.1). The structures were solved by direct-phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2 .^[32] All nonhydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. A summary of selected crystallographic data is provided in the section 3.5.1.

3.4.1. Synthesis of Amidinato Silylene-Borane Adducts

Synthesis of 3.36: $[\text{BH}_3 \cdot \text{THF}]$ (1.0 M in THF, 9.0 mL, 1.2 equiv.) was added to a solution of **3.33** (3.17 g, 7.5 mmol, 1.0 equiv.) in toluene (30 mL) at ambient temperature. The mixture was allowed to stir and the solution changed from clear orange to cloudy yellow after 16 hours. Upon filtration and concentration, colourless crystals of **3.36** were obtained.

Yield: 2.58 g (79%); M.p. 244-246 °C.

^1H NMR (395.9 MHz, C_6D_6 , 25.1 °C): δ 0.40 (s, 9H, SiMe_3), 0.68 (s, 9H, SiMe_3), 1.20 (s, 18H, $t\text{Bu}$), 6.83-6.93 (m, 3H, Ph), 7.13-7.14 (m, 1H, Ph), 7.22-7.24 (m, 1H, Ph) ppm, H_B signals were not detected.

$^{11}\text{B}\{^1\text{H}\}$ NMR (127.0 MHz, C_6D_6 , 25.4 °C): δ -38.18 (s) ppm.

^{11}B NMR (128.2 MHz, C_6D_6 , 25.3 °C): δ -38.17 (q, $^1J_{\text{B-H}} = 91.3$ Hz) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, C_6D_6 , 25.2 °C): δ 5.44, 5.92 (SiMe_3), 31.40 (CMe_3), 55.17 (CMe_3), 128.86, 130.62, 131.69 (Ph), 169.82 (NCN) ppm.

$^{29}\text{Si}\{^1\text{H}\}$ NMR (79.4 MHz, C_6D_6 , 25.1 °C): δ 4.54 (SiMe_3), 9.08 (SiMe_3), 22.05 (q, $^1J_{\text{Si-B}} = 67.1$ Hz, Si/B) ppm.

HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{45}\text{BN}_3\text{Si}_3$: 434.3014 $[(M+H)]^+$; found: 434.3010.

Synthesis of 3.37: $[\text{BH}_3 \cdot \text{THF}]$ (1.0 M in THF, 5.0 mL, 1.0 equiv.) was added to a solution of **3.34** (1.52 g, 5.00 mmol, 1.0 equiv.) in toluene (30 mL) at ambient temperature. The mixture was allowed to stir and the solution changed from clear orange to pale yellow after 16 hours. Upon filtration and concentration, colourless crystals of **3.37** were obtained.

Yield: 1.16 g (73%); M.p. 128-130 °C.

^1H NMR (395.9 MHz, C_6D_6 , 25.1 °C): δ 1.05 (s, 18H, $t\text{Bu}$), 2.70 (s, 6H, NMe_2), 6.78-6.92 (m, 5H, Ph) ppm, H_B signals were not detected.

$^{11}\text{B}\{^1\text{H}\}$ NMR (127.0 MHz, C_6D_6 , 25.4 °C): δ -46.89 (s) ppm.

^{11}B NMR (127.0 MHz, C_6D_6 , 25.3 °C): δ -46.89 (q, $^1J_{\text{B-H}} = 91.1$ Hz) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, C_6D_6 , 24.4 °C): δ 31.14 (CMe_3), 37.78 (NMe_2), 54.03 (CMe_3), 129.00, 130.45, 131.81 (Ph), 171.89 (NCN) ppm.

$^{29}\text{Si}\{^1\text{H}\}$ NMR (78.7 MHz, C_6D_6 , 24.7 °C): δ 30.24 (br, Si/B) ppm.

HRMS (ESI): m/z calcd for $\text{C}_{17}\text{H}_{33}\text{BN}_3\text{Si}$: 318.2537 $[(M+H)]^+$; found: 318.2547.

3.4.2. Synthesis of Amidinato Silylene-Monotriflate Boranes

Synthesis of 3.39: A solution of MeOTf (0.755 g, 0.50 mL, 4.60 mmol, 1.0 equiv.) in toluene (10 mL) was added to a solution of **3.36** (2.00 g, 4.60 mmol, 1.0 equiv.) in toluene (30 mL) at ambient temperature. The mixture was allowed to stir and solution changed from clear to cloudy after 16 hours with slight bubbling. Upon filtration and concentration, colourless crystals of **3.39** were obtained. Washing with hexanes provided a pure sample of **3.39** for spectroscopic analyses.

Yield: 2.45 g (92%); M.p. 162-166 °C.

^1H NMR (399.5 MHz, C_6D_6 , 23.7 °C): δ 0.27 (s, 9H, SiMe_3), 0.36 (s, 9H, SiMe_3), 1.12 (s, 18H, $t\text{Bu}$), 6.86-7.07 (m, 4H, Ph), 8.04-8.06 (m, 1H, Ph) ppm, H_B signals were not detected.

$^{11}\text{B}\{^1\text{H}\}$ NMR (127.0 MHz, C_6D_6 , 24.5 °C): δ -9.76 (br) ppm.

$^{13}\text{C}\{^1\text{H}\}$ (100.6 MHz, C_6D_6 , 27.0 °C): δ 5.06 (SiMe_3), 31.23 (CMe_3), 55.67 (CMe_3), 127.30, 129.38, 130.17, 131.27 (Ph), 173.49 (NCN) ppm, C_F signal was not detected.

^{19}F NMR (375.9 MHz, C_6D_6 , 23.7 °C): δ -74.50 (s) ppm.

$^{29}\text{Si}\{^1\text{H}\}$ NMR (79.4 MHz, C_6D_6 , 24.3 °C): δ 7.00, 10.76 (SiMe_3) ppm, Si_B signal was not detected.

HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{44}\text{BF}_3\text{N}_3\text{O}_3\text{SSi}_3$: 582.7322 [$(M+H)$] $^+$; found: 582.7333.

Synthesis of 3.40: A solution of MeOTf (0.336 g, 0.22 mL, 2.05 mmol, 1.0 equiv.) in toluene (10 mL) was added to a solution of **3.37** (0.65 g, 2.05 mmol, 1.0 equiv.) in toluene (20 mL) at ambient temperature. The mixture was allowed to stir and solution changed from clear to cloudy after 16 hours with slight bubbling. Upon filtration and concentration, colourless crystals of **3.40** were obtained.

Yield: 0.66 g (69%); M.p. 144-150 °C.

^1H NMR (395.9 MHz, C_6D_6 , 24.4 °C): δ 1.00 (s, 18H, tBu), 2.35 (s, 6H, NMe_2), 6.66-6.92 (m, 4H, Ph), 7.58-7.60 (m, 1H, Ph) ppm, H_B signals were not detected.

$^{11}\text{B}\{^1\text{H}\}$ NMR (127.0 MHz, C_6D_6 , 25.1 °C): δ -11.44 (br) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6 , 25.1 °C): δ 30.86 (CMe_3), 37.25 (NMe_2), 54.55 (CMe_3), 129.12, 129.40, 130.41, 131.12 (Ph), 176.24 (NCN) ppm, C_F signal was not detected.

^{19}F NMR (372.5 MHz, C_6D_6 , 24.5 °C): δ -75.39 (s) ppm.

Si_B signal was not detected.

HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{32}\text{BF}_3\text{N}_3\text{O}_3\text{SSi}$: 466.4222 [$(\text{M}+\text{H})$] $^+$; found: 466.4215.

Synthesis of 3.41: MeOTf (0.164 g, 0.11 mL, 1.00 mmol, 1.0 equiv.) was added to a solution of **3.38** (0.308 g, 1.00 mmol, 1.0 equiv) in toluene (20 mL) at ambient temperature. The mixture was allowed to stir and solution changed from clear to cloudy after 16 hours with slight bubbling. The volatiles were removed under *vacuo* and the pale yellow residue washed with hexane to afford **3.41** as a white powder.

Yield: 0.36 g (80%); M.p. 151-152 °C.

Yield: 0.36 g (80%); M.p. 151-152 °C.

^1H NMR (395.9 MHz, C_6D_6 , 24.3 °C): δ 1.02 (s, 18H, tBu), 6.69-6.97 (m, 4H, Ph), 7.44-7.47 (m, 1H, Ph) ppm, H_B signals were not detected.

$^{11}\text{B}\{^1\text{H}\}$ NMR (127.0 MHz, C_6D_6 , 24.6 °C): δ -11.15 (br) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6 , 25.2 °C): δ 30.80 (CMe_3), 56.08 (CMe_3), 127.19, 127.53, 130.83, 130.96, 131.68, 131.76 (Ph), 179.34 (NCN) ppm, C_F signal was not detected.

^{19}F NMR (372.5 MHz, C_6D_6 , 24.6 °C): δ -75.82 (s) ppm.

Si_B signal was not detected.

HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{26}\text{BClF}_3\text{N}_2\text{O}_3\text{SSi}$: 457.1167 [$(\text{M}+\text{H})$] $^+$; found: 457.1151.

3.4.3. Synthesis of Acyclic Amidinato Silylene-Boronium Cations

Synthesis of **3.42**:

Method A: Toluene (20 mL) was added to a mixture of **3.39** (0.581 g, 1.00 mmol, 1.0 equiv.) and **3.34** (0.303 g, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux overnight. Single crystals of **3.42** were grown from a saturated solution in a THF/hexane (ca. 1:1) mixture. Yield: 0.65 g (73%).

Method B: Toluene (20 mL) was added to a mixture of **3.40** and **3.33**. The reaction mixture was heated under reflux overnight. Upon cooling, all solvents were removed in *vacuo* and the residue washed with hexane to afford colourless crystalline solids of **3.42**. Yield: 0.67 g (75%).

M.p. 225-230 °C.

^1H NMR (395.9 MHz, THF- d_8 , 24.5 °C): δ 0.52 (s, 9H, SiMe₃), 0.56 (s, 9H, SiMe₃), 1.25 (s, 18H, *t*Bu), 1.34 (s, 18H, *t*Bu), 2.86 (s, 6H, NMe₂), 7.38-7.83 (m, 10H, Ph) ppm, H_B signals were not detected.

$^{11}\text{B}\{^1\text{H}\}$ NMR (127.0 MHz, THF- d_8 , 24.9 °C): δ -45.93 (s) ppm.

^{11}B NMR (127.0 MHz, THF- d_8 , 24.9 °C): δ -45.93 (t, $^1J_{\text{B-H}} = 81.4$ Hz) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (99.5 MHz, THF- d_8 , 25.2 °C): δ 6.15, 7.36 (SiMe₃), 31.63, 31.76 (CMe₃), 39.41 (NMe₂), 55.41, 56.54 (CMe₃), 128.27, 128.67, 129.20, 129.51, 129.67, 130.30, 130.60, 130.75, 130.89, 132.29, 132.71 (Ph), 175.42, 177.76 (NCN) ppm, C_F signal was not detected.

^{19}F NMR (372.5 MHz, C₆D₆, 24.6 °C): δ -78.67 (s) ppm.

$^{29}\text{Si}\{^1\text{H}\}$ NMR (78.7 MHz, THF- d_8 , 24.9 °C): δ 6.70 (SiMe₃), 8.71 (SiMe₃) ppm, Si_B signals were not detected.

HRMS (ESI): m/z calcd for C₃₈H₇₂BN₆Si₄: 735.4989 [(M-OTf)]⁺; found: 735.4977.

Synthesis of **3.43**:

Method A: Toluene (20 mL) was added to a mixture of **3.39** (0.580 g, 1.00 mmol, 1.0 equiv.) and **3.35** (0.294, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux overnight. Upon filtration and concentration, colourless crystals of **3.43** were obtained. Yield: 0.59 g (67%).

Method B: Toluene (20 mL) was added to a mixture of **3.41** (0.457 g, 1.00 mmol, 1.0 equiv.) and **3.33** (0.420, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux overnight. The solvent was removed in vacuo and the residue washed with hexane to afford colourless crystalline solids of **3.43**. Yield: 0.57 g (65%).

M.p. 231 °C (dec).

^1H NMR (399.5 MHz, THF- d_8 , 22.5 °C): δ 0.52 (s, 9H, SiMe₃), 0.53 (s, 9H, SiMe₃), 1.31 (s, 18H, tBu), 1.34 (s, 18H, tBu), 7.61-7.78 (m, 10H, Ph) ppm, H_B signals were not detected.

$^{11}\text{B}\{^1\text{H}\}$ NMR (128.2 MHz, THF- d_8 , 22.9 °C): δ -44.86 (s) ppm.

^{11}B NMR (128.2 MHz, THF- d_8 , 22.8 °C): δ -44.85 (t, $^1J_{\text{B-H}} = 83.8$ Hz) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, THF- d_8 , 22.9 °C): δ 6.06, 6.84 (SiMe₃), 31.68, 31.79 (CMe₃), 56.59, 57.29 (CMe₃), 126.22, 128.71, 129.08, 129.17, 129.58, 129.84, 130.42, 132.72, 132.95 (Ph), 176.23, 181.24 (NCN) ppm, C_F signal not detected.

^{19}F NMR (375.9 MHz, THF- d_8 , 22.6 °C): δ -80.72 (s) ppm.

$^{29}\text{Si}\{^1\text{H}\}$ NMR (78.7 MHz, THF- d_8 , 24.6 °C): δ 7.31, 9.72 (SiMe₃), Si_B signals were not detected.

HRMS (ESI): m/z calcd for C₃₆H₆₆BCIN₅Si₄: 726.4177 [(M-OTf)]⁺; found: 726.4170.

Synthesis of 3.44: Toluene (20 mL) was added to a mixture of **3.40** (0.465 g, 1.00 mmol, 1.0 equiv.) and **3.34** (0.303 g, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux overnight. Crystalline solids of **3.44** were formed from a saturated solution in a THF/hexane (ca. 1:1) mixture.

Yield: 0.69 g (90%); M.p. 235 °C (dec).

^1H NMR (395.9 MHz, THF- d_8 , 25.5 °C): δ 1.23 (s, 36H, $t\text{Bu}$), 2.81 (s, 12H, NMe_2), 7.47-7.76 (m, 10H, Ph) ppm, H_B signals were not detected.

$^{11}\text{B}\{^1\text{H}\}$ NMR (127.0 MHz, THF- d_8 , 25.9 °C): δ -51.94 (s) ppm.

^{11}B NMR (127.0 MHz, THF- d_8 , 25.8 °C): δ -51.95 (t, $^1J_{\text{B-H}} = 84.4$ Hz) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, THF- d_8 , 25.7 °C): δ 31.41 (CMe_3), 38.55 (NMe_2), 55.37 (CMe_3), 128.79, 129.57, 129.67, 130.24, 132.36 (Ph), 177.47 (NCN) ppm.

^{19}F NMR (372.5 MHz, C_6D_6 , 25.6 °C): δ -78.99 (s) ppm.

Si_B signals were not detected.

HRMS (ESI): m/z calcd for $\text{C}_{34}\text{H}_{60}\text{BN}_6\text{Si}_2$: 619.4511 [$(\text{M}-\text{OTf})$] $^+$; found: 619.4502.

Synthesis of 3.45: Toluene (20 mL) was added to a mixture of **3.39** (0.581 g, 1.00 mmol, 1.0 equiv.) and DMAP (0.122 g, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux overnight. Pale yellow residue formed upon cooling of the reaction mixture to ambient temperature. The residue was confirmed to be **3.45** by ^1H NMR. Single crystals were grown from a saturated solution in a toluene/THF (ca. 1:1) mixture.

Yield: 0.58 g (83%); M.p. 210 °C (dec).

^1H NMR (395.9 MHz, C_6D_6 , 25.1 °C): δ 0.27 (s, 9H, SiMe_3), 0.43 (s, 9H, SiMe_3), 0.97 (s, 18H, $t\text{Bu}$), 2.42 (s, 6H, NMe_2), 6.91-6.96 (m, 4H, Ph), 7.91-8.08 (m, 5H, Ph) ppm, H_B signals were not detected.

$^{11}\text{B}\{^1\text{H}\}$ NMR (127.0 MHz, C_6D_6 , 25.5 °C): δ -15.74 (br) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, $\text{THF}-d_8$, 27.8 °C): δ 5.70, 5.99 (SiMe_3), 31.51 (CMe_3), 40.06 (NMe_2), 56.29 (CMe_3), 108.72, 109.72, 127.95, 129.08, 129.82, 130.19, 131.30, 132.44, 146.96, 147.46, 156.91 (Ph), 175.58 (NCN) ppm, C_F signal was not detected.

^{19}F NMR (372.5 MHz, C_6D_6 , 24.9 °C): δ -77.36 (s) ppm.

$^{29}\text{Si}\{^1\text{H}\}$ NMR (78.7 MHz, $\text{THF}-d_8$, 25.4 °C): δ 6.84, 9.78 (SiMe_3) ppm, Si_B signal was not detected.

HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{53}\text{BN}_5\text{Si}_3$: 554.3702 [$(\text{M}-\text{OTf})$] $^+$; found: 554.3705.

3.4.4. Synthesis of Endocyclic Amidinato Silylene-Boronium Cations

Synthesis of 3.46: Toluene (20 mL) was added to a mixture of **3.39** (0.581 g, 1.00 mmol, 1.0 equiv.) and **3.33** (0.419 g, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux overnight. Slow evaporation of the solvent, or gradual cooling to room temperature, afforded block-like colourless crystals of **3.46**.

Yield: 0.509 g (51%); M.p. 229 °C (dec).

^1H NMR (395.9 MHz, THF- d_8 , -89.9 °C): δ 0.28 (s, 2H, CH_2), 0.45 (s, 9H, SiMe_3), 0.49 (s, 6H, SiMe_2), 0.55 (s, 9H, SiMe_3), 0.59 (s, 9H, SiMe_3), 1.30 (m, 36H, $t\text{Bu}$), 7.60–7.80 (m, 10H, Ph) ppm, H_B signal was not detected.

$^{11}\text{B}\{^1\text{H}\}$ NMR (127.0 MHz, THF- d_8 , 26.0 °C): δ -32.99 (s) ppm.

^{11}B NMR (127.0 MHz, THF- d_8 , 24.4 °C): δ -33.01 (d, $^1J_{\text{B-H}} = 77.7$ Hz) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_2Cl_2 , 27.3 °C): δ 1.33, 4.74, 6.57, 7.64 (SiMe_n), 31.76, 32.06, 32.09, 32.27 (CMe_3), 55.54, 55.59, 56.43, 56.72 (CMe_3), 127.41, 127.99, 128.30, 128.66, 129.23, 129.28, 129.37, 129.79, 130.12, 131.97, 132.15 (Ph), 174.04, 176.94 (NCN) ppm, C_F signal was not detected.

^{19}F NMR (372.5 MHz, THF- d_8 , 25.8 °C): δ -78.80 (s) ppm.

$^{29}\text{Si}\{^1\text{H}\}$ NMR (78.7 MHz, THF- d_8 , 24.5 °C): δ 4.22, 7.12, 8.17, 17.70 (SiMe_n) ppm, Si_B signals were not detected.

HRMS (ESI): m/z calcd for $\text{C}_{42}\text{H}_{82}\text{BN}_6\text{Si}_6$: 849.5310 [$(\text{M-OTf})^+$]; found: 849.5308.

Synthesis of 3.49: Toluene was added to a mixture of **3.35** (0.294 g, 1.00 mmol, 1.0 equiv.) and [LLi] (L = PhC(NtBu)₂; 0.238g, 1.00 mmol, 1.0 equiv.). The reaction mixture was allowed to stir at room temperature for 16 hours. Upon filtration and concentration, colourless crystals of **3.49** were

obtained.

Yield: 0.39 g (80%); M.p. 121-123 °C.

¹H NMR (395.9 MHz, C₆D₆, 25.9 °C): δ 1.12 (s, 18H, tBu), 1.22 (s, 9H, tBu), 2.06 (s, 9H, tBu), 6.85-7.11 (m, 7H, Ph), 7.36 (d, ³J_{H-H} = 7.7 Hz, 1H, Ph), 7.49 (d, ³J_{H-H} = 7.2 Hz, 2H, Ph) ppm.

¹³C{¹H} NMR (99.5 MHz, C₆D₆, 26.1 °C): δ 31.91, 33.22, 33.61 (CMe₃), 53.74, 54.82, 58.48 (CMe₃), 127.63, 127.77, 129.27, 129.62, 144.65 (Ph), 157.83, 160.20 (NCN) ppm.

²⁹Si{¹H} NMR (78.7 MHz, C₆D₆, 26.0 °C): δ -23.14 (s) ppm.

HRMS (ESI): *m/z* calcd for C₃₀H₄₇N₄Si: 491.3570 [(*M*+*H*)⁺]; found: 491.3559.

Synthesis of 3.50: Toluene (20 mL) was added to a mixture of **3.39** (0.581 g, 0.99 mmol, 1.0 equiv.) and **3.49** (0.490 g, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux overnight. Colourless crystals of **3.50** were obtained from a saturated solution in a toluene/PhF (ca. 1:1) mixture.

Yield: 0.71 g (66%); M.p. 201 °C (dec).

¹H NMR (395.9 MHz, THF-*d*₈, 27.3 °C): δ 0.47 (s, 2H, CH₂), 0.52 (s, 6H, SiMe₂), 0.53 (s, 9H, SiMe₃), 1.30 (s, 18H, tBu), 1.31 (s, 18H, tBu), 1.34 (s, 18H, tBu), 1.35 (s, 18H, tBu), 7.60-7.70 (m, 15H, Ph) ppm, H_B signal was not detected.

¹¹B{¹H} NMR (127.0 MHz, THF-*d*₈, 27.2 °C): δ -38.64 (s) ppm.

¹¹B NMR (127.0 MHz, THF-*d*₈, 26.8 °C): δ -38.66 (d, ¹J_{B-H} = 81.4 Hz) ppm.

¹³C{¹H} NMR (100.6 MHz, THF-*d*₈, 27.4 °C): δ 6.28, 7.70 (SiMe_n), 31.31, 31.90, 32.01, 32.34 (CMe₃), 56.81, 57.38, 57.52, 57.79 (CMe₃), 129.29, 129.59, 129.69, 130.06, 130.97, 132.31, 132.94, 133.13 (Ph), 176.46, 181.51 (NCN) ppm, C_F signal was not detected.

¹⁹F NMR (372.5 MHz, THF-*d*₈, 25.8 °C): δ -78.80 (s) ppm.

²⁹Si{¹H} NMR (78.7 MHz, THF-*d*₈, 24.5 °C): δ 8.75, 4.21 (SiMe_n) ppm, Si_B signals were not detected.

HRMS (ESI): *m/z* calcd for C₅₁H₈₇BN₇Si₄: 920.6193 [(*M*-OTf)⁺]; found: 920.6188.

Synthesis of 3.52: Toluene (20 mL) was added to a mixture of **3.39** (0.580 g, 0.99 mmol, 1.0 equiv.) and **3.51** (0.388, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux overnight. Upon cooling to room temperature, **3.52** was crystallized from a saturated solution in a THF/hexane (ca. 1:1) mixture together with [**3.51**•HOTf].

Yield: 0.32 g (34%); M.p. 242 °C (dec).

^1H NMR (399.5 MHz, THF- d_8 , 22.5 °C): δ 0.21 (s, 2H, CH_2), 0.27 (s, 9H, SiMe_3), 0.74 (s, 9H, $t\text{Bu}$), 0.90 (s, 6H, SiMe_2), 1.09 (s, 9H, $t\text{Bu}$), 1.16 (d, $^3J_{\text{H-H}} = 6.0$ Hz, 6H, CHMe_2), 1.23 (d, $^3J_{\text{H-H}} = 6.4$ Hz, 6H, CHMe_2), 1.40 (d, $^3J_{\text{H-H}} = 6.4$ Hz, 6H, CHMe_2), 1.48 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6H, CHMe_2), 2.65 (sept, $^3J_{\text{H-H}} = 6.4$ Hz, 6H, CHMe_2), 2.95 (sept, $^3J_{\text{H-H}} = 6.4$ Hz, 6H, CHMe_2), 7.43-7.71 (m, 11H, Ph), 7.73 (s, 2H, $=\text{CH}$) ppm, H_B signal was not detected.

$^{11}\text{B}\{^1\text{H}\}$ NMR (128.2 MHz, THF- d_8 , 23.0 °C): δ -28.54 (s) ppm.

^{11}B NMR (128.2 MHz, THF- d_8 , 22.9 °C): δ -28.59 (d, $^1J_{\text{B-H}} = 78.3$ Hz) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, THF- d_8 , 25.8 °C): δ 4.85, 5.66, 14.58 (SiMe_n), 23.17, 23.68, 26.21, 26.55 (CHMe_2), 30.10, 30.68 (CHMe_2), 31.80, 31.95 (CMe_3), 54.88, 56.30 (CMe_3), 125.52 ($=\text{CH}$), 126.75, 127.62, 128.31, 128.94, 129.75, 130.07, 130.21, 132.10, 136.25, 146.79 (Ph), 177.40 (NCN) ppm, C_F signal was not detected.

^{19}F NMR (372.5 MHz, THF- d_8 , 25.8 °C): δ -78.98 (s) ppm.

$^{29}\text{Si}\{^1\text{H}\}$ NMR (78.7 MHz, THF- d_8 , 24.5 °C): δ 9.15, 8.10 (SiMe_n) ppm, Si_B signal was not detected.

HRMS (ESI): m/z calcd for $\text{C}_{48}\text{H}_{77}\text{BN}_5\text{Si}_3$: 818.5580 [(M-OTf)] $^+$; found: 818.5561.

3.4.5. Reactivity of 3.46

Synthesis of 3.53: Toluene (20 mL) was added to a mixture of **3.46** (1.00 g, 1.00 mmol, 1.0 equiv.) and $[\text{NH}_3 \cdot \text{BH}_3]$ (0.031 g, 1.00 mmol, 1.0 equiv.) at ambient temperature. The reaction mixture was allowed to stir for 6 hours and the solution changed from light orange to a pale yellow suspension. Upon filtration, the residue was dried to afford **3.53** as a white powder.

Yield: 0.054 g (11%); M.p. 189-191 °C.

^1H NMR (399.5 MHz, $\text{THF-}d_8$, 22.5 °C): δ 0.57 (s, 9H, SiMe_3), 0.61 (s, 9H, SiMe_3), 1.32 (s, 18H, $t\text{Bu}$), 5.32 (br s, 1H, SiH), 7.63-7.71 (m, 5H, Ph) ppm.

^{19}F NMR (372.5 MHz, $\text{THF-}d_8$, 25.8 °C): δ -77.72 (s) ppm.

HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{42}\text{N}_3\text{Si}_3$: 420.2687 $[(M-\text{OTf})]^+$; found: 420.2667.

3.5 Appendices

3.5.1. Crystallographic Data

Compound	3.36	3.37	3.38	3.39
Formula	C ₂₁ H ₄₄ BN ₃ Si ₃	C ₁₇ H ₃₂ BN ₃ Si	C ₁₅ H ₂₆ BClN ₂ Si	C ₂₂ H ₄₃ BF ₃ N ₃ O ₃ SSi ₃
<i>M</i>	433.67	317.35	308.73	581.73
<i>T</i> / K	133(2)	103(2)	100(2)	296(2)
Color	Colourless	Colourless	Colourless	Colourless
Crystal size / mm	0.220 x 0.310 x 0.420	0.020 x 0.080 x 0.120	0.080 x 0.100 x 0.120	0.100 x 0.140 x 0.300
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	<i>P</i> -1	<i>P</i> 1 21/ <i>n</i> 1	<i>P</i> 1 21/ <i>c</i> 1	<i>P</i> 1 21/ <i>n</i> 1
<i>a</i> / Å	13.9910(9)	11.611(2)	13.0319(8)	9.3828(14)
<i>b</i> / Å	14.0313(8)	13.273(2)	10.8574(6)	20.524(3)
<i>c</i> / Å	14.0422(8)	12.945(2)	12.9353(6)	17.091(2)
<i>α</i> / °	89.765(2)	90	90	90
<i>β</i> / °	81.800(2)	90.254(7)	92.5282(18)	97.892(5)
<i>γ</i> / °	81.396(2)	90	90	90
<i>V</i> / Å ³	2697.3(3)	1995.0(6)	1828.47(17)	3260.1(8)
<i>Z</i>	4	4	4	4
<i>d</i> _{calcd} / g cm ⁻³	1.068	1.057	1.121	1.185
<i>μ</i> / mm ⁻¹	0.187	0.118	0.267	0.253
<i>F</i> (000)	952	696	664	1240
Index ranges	-10 ≤ <i>h</i> ≤ 20	-15 ≤ <i>h</i> ≤ 15	-16 ≤ <i>h</i> ≤ 17	-11 ≤ <i>h</i> ≤ 11
	-20 ≤ <i>k</i> ≤ 19	-17 ≤ <i>k</i> ≤ 17	-14 ≤ <i>k</i> ≤ 14	-25 ≤ <i>k</i> ≤ 25
	-19 ≤ <i>l</i> ≤ 20	-16 ≤ <i>l</i> ≤ 17	-16 ≤ <i>l</i> ≤ 17	-21 ≤ <i>l</i> ≤ 21
No. of reflections collected	24737	24229	17407	46131
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2(<i>σ</i>)]	0.0623, 0.1276	0.0632, 0.1202	0.0522, 0.1098	0.0594, 0.1221
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1220, 0.1556	0.1402, 0.1479	0.1039, 0.1366	0.1634, 0.1624
Goodness-of-fit on <i>F</i> ²	0.98	1.008	1.023	0.998
Data / restraints / parameters	17055 / 15 / 553	4778 / 3 / 216	4336 / 122 / 237	6726 / 410 / 437
Largest diff. peak and hole/ e Å ⁻³	0.457 and -0.373	0.492 and -0.271	0.305 and -0.328	0.508 and -0.279

Compound	3.40	3.42	3.43	3.45
Formula	C ₁₈ H ₃₁ BF ₃ N ₃ O ₃ SSi	C ₃₉ H ₇₂ BF ₃ N ₆ O ₃ SSi ₄	C _{40.50} H ₇₀ BCIF ₃ N ₅ O ₃ SSi ₄	C ₂₉ H ₅₃ BF ₃ N ₅ O ₃ SSi ₃
<i>M</i>	465.42	885.25	922.69	703.9
<i>T</i> / K	103(2)	153(2)	103(2)	153(2)
Color	Colourless	Colourless	Colourless	Colourless
Crystal size / mm	0.240 x 0.300 x 0.420	0.180 x 0.240 x 0.300	0.120 x 0.200 x 0.220	0.020 x 0.060 x 0.080
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space Group	<i>P</i> 21 21 21	<i>P</i> 1 21/ <i>n</i> 1	<i>P</i> 1 21/ <i>n</i> 1	<i>P</i> 1 21/ <i>c</i> 1
<i>a</i> / Å	9.1976(6)	11.9235(6)	14.6988(3)	16.456(3)
<i>b</i> / Å	14.7250(11)	17.1562(8)	17.2249(3)	14.260(2)
<i>c</i> / Å	35.429(3)	24.4084(11)	19.8748(4)	16.178(2)
<i>α</i> / °	90	90	90	90
<i>β</i> / °	90	101.4190(12)	97.4640(13)	93.323(5)
<i>γ</i> / °	90	90	90	90
<i>V</i> / Å ³	4798.3(6)	4894.2(4)	4989.37(17)	3790.0(10)
<i>Z</i>	8	4	4	4
<i>d</i> _{calcd} / g cm ⁻³	1.289	1.201	1.228	1.234
<i>μ</i> / mm ⁻¹	0.231	0.216	2.412	0.231
<i>F</i>(000)	1968	1904	1972	1504
Index ranges	-13 ≤ <i>h</i> ≤ 12	-16 ≤ <i>h</i> ≤ 16	-17 ≤ <i>h</i> ≤ 17	-19 ≤ <i>h</i> ≤ 15
	-21 ≤ <i>k</i> ≤ 20	-23 ≤ <i>k</i> ≤ 23	-20 ≤ <i>k</i> ≤ 20	-17 ≤ <i>k</i> ≤ 16
	-50 ≤ <i>l</i> ≤ 49	-29 ≤ <i>l</i> ≤ 33	-23 ≤ <i>l</i> ≤ 23	-19 ≤ <i>l</i> ≤ 16
No. of reflections collected	35782	75835	38913	35172
<i>R</i>1, <i>wR</i>2 [<i>I</i> > 2(<i>σ</i>)]	0.0533, 0.1029	0.0516, 0.1383	0.0832, 0.2095	0.0678, 0.1123
<i>R</i>1, <i>wR</i>2 (all data)	0.0812, 0.1144	0.0935, 0.1828	0.1128, 0.2361	0.2196, 0.1620
Goodness-of-fit on <i>F</i> ²	1.017	1.095	1.058	0.986
Data / restraints / parameters	14524 / 6 / 569	13224 / 338 / 613	8811 / 442 / 640	6807 / 344 / 499
Largest diff. peak and hole/ e Å ⁻³	0.469 and -0.421	0.490 and -0.534	0.948 and -0.476	0.391 and -0.341

Compound	3.46	3.49	3.50	3.52
Formula	C ₅₇ H ₉₈ BF ₃ N ₆ O ₃ SSi ₆	C ₃₀ H ₄₆ N ₄ Si	C _{55.50} H ₉₁ BF ₃ N ₇ O ₃ SSi ₄	C _{59.50} H ₈₉ BF ₃ N ₅ O ₃ SSi ₃
<i>M</i>	1183.82	490.8	1116.58	1106.49
<i>T</i> / K	103(2)	103(2)	103(2)	103(2)
Color	Colourless	Colourless	Colourless	Colourless
Crystal size / mm	0.240 x 0.260 x 0.420	0.400 x 0.410 x 0.420	0.080 x 0.220 x 0.400	0.200 x 0.300 x 0.320
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space Group	C 1 2/c 1	<i>P b c a</i>	<i>P</i> 1 21/c 1	<i>P</i> 1 21/n 1
<i>a</i> / Å	20.6041(8)	14.6413(11)	18.089(3)	18.2442(6)
<i>b</i> / Å	14.7183(5)	14.0015(7)	14.010(2)	17.6271(5)
<i>c</i> / Å	21.6917(7)	29.006(2)	26.345(4)	20.4004(5)
α / °	90	90	90	90
β / °	92.596(2)	90	109.850(3)	106.7119(9)
γ / °	90	90	90	90
<i>V</i> / Å ³	6571.4(4)	5946.2(7)	6279.8(15)	6283.5(3)
<i>Z</i>	4	8	4	4
<i>d</i> _{calcd} / g cm ⁻³	1.197	1.096	1.181	1.17
μ / mm ⁻¹	0.212	0.103	0.182	0.163
<i>F</i> (000)	2552	2144	2404	2380
Index ranges	-29 ≤ <i>h</i> ≤ 29	-20 ≤ <i>h</i> ≤ 20	-21 ≤ <i>h</i> ≤ 21	-24 ≤ <i>h</i> ≤ 24
	-21 ≤ <i>k</i> ≤ 21	-13 ≤ <i>k</i> ≤ 20	-16 ≤ <i>k</i> ≤ 16	-23 ≤ <i>k</i> ≤ 23
	-31 ≤ <i>l</i> ≤ 27	-41 ≤ <i>l</i> ≤ 40	-31 ≤ <i>l</i> ≤ 31	-26 ≤ <i>l</i> ≤ 26
No. of reflections collected	55398	46681	80702	138003
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2(σ)]	0.0658, 0.1572	0.0591, 0.1281	0.0800, 0.1400	0.0720, 0.1586
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1193, 0.1896	0.1008, 0.1481	0.1740, 0.1703	0.1180, 0.1955
Goodness-of-fit on <i>F</i> ²	1.035	1.032	1.037	1.066
Data / restraints / parameters	10614 / 545 / 503	9125 / 0 / 328	11155 / 87 / 718	15157 / 762 / 841
Largest diff. peak and hole/ e Å ⁻³	1.105 and -0.500	0.594 and -0.264	1.046 and -0.471	0.944 and -0.630

3.5.2. NMR Spectra of New Compounds

3.36: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{11}B , ^{13}C , ^{29}Si

3.37: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{11}B , ^{13}C , ^{29}Si

3.39: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{13}C , ^{19}F , ^{29}Si

3.40: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{13}C , ^{19}F

3.41: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{13}C , ^{19}F

3.42: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{11}B , ^{13}C , ^{19}F , ^{29}Si

3.43: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{11}B , ^{13}C , ^{19}F , ^{29}Si

3.44: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{11}B , ^{13}C , ^{19}F

3.45: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{13}C , ^{19}F , ^{29}Si

3.46: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{11}B , ^{13}C , ^{19}F , ^{29}Si

3.46-d: $^{11}\text{B}\{^1\text{H}\}$, ^{11}B (THF- d_8 , quartz NMR tube)

3.49: ^1H , ^{13}C , ^{29}Si

3.50: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{11}B , ^{13}C , ^{19}F , ^{29}Si

¹¹B

X : parts per Million : 11B

¹³C{¹H}

3.52: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{11}B , ^{13}C , ^{19}F , ^{29}Si

¹¹B

¹³C{¹H}

3.53: ^1H , ^{19}F

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CHAPTER 4:

B–H Activation by an Amidinato Amidosilylene: Non-Innocent Amidinate Ligand[‡]

4.1 Introduction

The seeming ease of low valent main group element compounds to activate small molecules is commonly attributed to their ambiphilic character; that is, their ability to simultaneously act as a nucleophile and electrophile. In the case of group 14, both homonuclear^[1] $[L_2E:]$ (E = low valent group 14 element, L = supporting ligand) and binuclear^[2] $[LE\equiv EL]$ or $[LE:]_2$ possess readily accessible HOMOs (nucleophilic) and LUMOs (electrophilic) which can be exploited for such reactivity. Specifically, the homolytic cleavage of substrates by a single low valent main group center is achieved in a manner evocative of that boasted by transition metals.^[3] Most importantly, it involves the acceptance of HOMO (or filled d orbitals) electrons into the anti-bonding orbital (σ^*) of the concerned bond, with a concomitant donation of its bonding (σ) electrons to the LUMO (or empty d orbitals).^[4] This double electron transfer with dihydrogen as an example is represented in Chart 4.1.^[4]

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Chart 4.1 Schematic illustration of dihydrogen activation by (a) a low valent group 14 element center; and (b) a transition metal center.

By analogy, H–Y bonds (Y = N, O, Si, P) in small molecules such as H₂O, NH₃, HSiR₃ and HPR₂ can also be oxidatively added across the active center. Proof of this theory was available as early as 2007, in which cyclic alkyl(amino)carbenes (cAACs) such as **4.1** and **4.2** are efficient in inserting into the N–H bond of NH₃ (Scheme 4.1a).^[4] Subsequently in 2010, they realized the same task with silanes PhSiH₃ and phosphanes PhPH₂ and HPPH₂.^[5] More recently, bis(boryl)stannylene **4.3** has been demonstrated to react with a series of protic (Y = N, O) and hydridic (Y = Si) Y–H bonds to afford the corresponding adducts **4.3-HY** (Scheme 4.1b).^[6] With phosphine-stabilized silylenes **4.4** and **4.5**, their interactions with Si–H and P–H bonds are facile, and remarkably reversible (Scheme 4.1c).^[7]

Scheme 4.1 Oxidative addition of H–Y bonds onto low valent group 14 element centers.

Contrastingly, the activation of B–H bonds is rare. While its dissociation energy (for example, three-coordinate boron, BH₃: 105.5 kcal/mol; catecholborane (HBcat): 111.3 kcal/mol; four-coordinate boron, NH₃BH₃: 102.6 kcal/mol) is comparable to that of H–H (104.2 kcal/mol), this value remains rather impervious to substituent effects.^[8] Furthermore, substances capable of cleaving the latter do not necessarily also cleave the former, especially with Lewis acidic BH₃. Namely, H₂-splitting cAACs **4.1** and **4.2** can only cleave the B–H bond in pinacolborane (HBpin) to generate **4.1/2-HBpin**, while a stable Lewis acid-base adduct **4.1-BH₃** is furnished in the presence of BH₃ (Scheme 4.2a).^[5] Likewise, bis(boryl)stannylene **4.3** is only competent in activating B–H in amino-substituted BH₃•NMe₃ (Scheme 4.2b).^[6]

Scheme 4.2 Reaction of (a) cAACs; and (b) stannylene with H–H and H–B bonds.

The apparent difficulty of this activation was highlighted by Mezáilles and our group in 2013.^[9] An efficient two-electron transfer (Chart 4.1) is imperative for the formation of new E–H and E–BH₂ bonds at the low valent main group center (E). However, donation of electron density from the filled s orbital (lone pair electrons) of E into the empty p at B is the favoured mode of interaction (Chart 4.2a, left), rather than into the empty σ^* of B–H (Chart 4.2a, right). The reverse donation of B–H σ electrons into the empty p orbital on E is also poor, due to its weak nucleophilicity, not to mention the ineffective overlap of orbitals (Chart 4.2b). This often results in the simple coordination of the BH₃ moiety to the active E center and indicates that B–H activation by E is synthetically challenging.

Chart 4.2 Orbital interactions between low valent group 14 element center and B–H bond.

Until now, the activation of B–H bond in non-amino stabilized BH_3 by main group compounds is exceedingly limited. It can only be accomplished by carbenoids^[9] and N,N' -diamidocarbenes (DACs)^[10] that feature pronounced nucleophilic and electrophilic character. As shown in Scheme 4.3a, the B–H of $\text{BH}_3 \cdot \text{SMe}_2$ adds oxidatively across the carbene center of carbenoid **4.6** to yield a solvent-stabilized adduct **4.6-BH₃**.^[9] In the same report, the groups of Mezáilles and So also noted that borane-containing carbenoid **4.7**, generated from germinal dianionic species **4.7A**, affords the B–H inserted **4.7-BH₃** via a possibly intermolecular pathway.^[9] In 2016, Bielawski discovered that DAC **4.8** reacts similarly to give **4.8-BH₃**.^[10] Interestingly, the initial product appears unstable in all cases; **4.6/4.7-BH₃** dimerize to **4.6/4.7-BH₃'** respectively,^[9] whereas a ring expansion is observed with **4.8-BH₃** into **4.8-BH₃'** (Scheme 4.3).^[10]

Scheme 4.3 Activation of B–H in BH₃·SMe₂ by (a) carbenoids; and (b) a DAC.

Although *N*-heterocyclic carbenes (NHCs) are typically regarded as spectator ligands, the conversion of **4.8-BH₃** into **4.8-BH₃'** is in line with previous studies. In 2012, the groups of Radius,^[11] Rivard,^[12] and Hill^[13] independently established that NHC **4.9** and NHC derivatives **4.10** and **4.11** undergo sequential oxidative addition, ring expansion and hydride migration with Si–H (Scheme 4.4a), B–H (Scheme 4.4b) and Be–H (Scheme 4.4c) respectively to give the corresponding six-membered rings **4.9'** to **4.11'**.

Scheme 4.4 Ring expansion of NHCs and its derivatives with (a) H–Si; (b) H–B; and (c) H–Be bonds.

As *N*-Heterocyclic silylenes (NHSis) are largely analogous to their lighter congeners, whereby both classes of compounds are proficient in stabilizing main group elements in oxidation state zero and excellent ligands to transition metals in homogenous catalysis, we envisage that NHSis will exhibit similar behavior to NHCs in the presence of H–Y bonds. Moreover, since amidinato low-valent silicon compounds have delivered positive results in terms of coordination chemistry (see Chapters 1 and 2 for details) and small molecule activation (see Chapter 3 for details), we were interested in investigating the feasibility of these compounds toward B–H bond activation. Herein, we describe the B–H bond activation of boranes by amidinato amidosilylene [L{(SiMe₃)(Ar)N}Si:] (**4.12**; L = PhC(NtBu)₂, Ar = 2,6-*i*PrC₆H₃).

4.2 Results and Discussion

4.2.1 Synthesis of Amidinato Amidosilylene (4.12)

Based on the fascinating $C(sp^3)-H$ borylation and H_2 activation outlined in the previous chapter, we were excited to generalize these reactions with other bulky silylene boranes. Hence, we set out to synthesize an amidinato silylene with marked steric hindrance. Treatment of the versatile amidinato chlorosilylene $[L(Cl)Si:]^{[14]}$ ($L = PhC(NtBu)_2$) with equimolar lithium amide $[LiN(SiMe_3)Ar]^{[15]}$ ($Ar = 2,6\text{-}iPr_2C_6H_3$) in toluene at ambient temperature afforded the targeted amidinato amidosilylene **4.12** overnight (Scheme 4.5). The by-product, LiCl, was filtered off and volatiles removed under vacuum to yield a yellowish powder of **4.12** (92%) upon washing with hexane.

Scheme 4.5 Synthesis of amidinato amidosilylene **4.12**.

Colourless crystals of **4.12** were harvested from a saturated toluene solution stored at 0 °C for 3 days. As shown in Figure 4.1, the Si1 atom is tricoordinated by two amidinate N donors and one amido ligand. The sum of bond angles around Si1 (281.82°) resembles that of other amidinato amidosilylenes $[L(NR_2)Si:]$ ($R = Me$,^[16] 274.5°; $R = SiMe_3$,^[17] 289.59°) and its distorted trigonal pyramidal geometry corroborates the existence of a stereoactive lone pair. Si–N(amidinate) bond lengths in this case are typical at 1.932(2) and 1.926(2) Å,^[14,16,17] while the Si–N(amido) bond length of 1.785(2) Å indicates it is a single bond.

Figure 4.1 ORTEP drawing of **4.12** with thermal ellipsoids at 30% probability level. As there are two independent molecules in the asymmetric unit with slightly different bond lengths and angles, only one independent molecule is discussed here for clarity. For the same reason, hydrogen atoms and solvent molecules are elided. Selected bond lengths (Å) and bond angles (°): Si1-N1 1.932(2), Si1-N2 1.926(2), Si1-N3 1.785(2), C5-N1 1.341(3), C5-N2 1.342(3); N1-Si1-N2 67.80(9), N2-Si1-N3 106.88(9), N3-Si1-N1 107.14(9), N1-C5-N2 106.7(2).

Compound **4.12** is excellently soluble in toluene, THF and benzene. It was fully characterized by multinuclear NMR spectroscopy. In a C_6D_6 solution, the two *t*Bu substituents on the amidinate backbone share a common signal in the 1H NMR at δ 1.29 ppm; this singlet is downfield shifted compared to its precursor (δ 1.08 ppm).^[14] Regarding the amido ligand, the $SiMe_3$ group resonates at δ 0.33 (s) ppm; two doublets at δ 1.37 ($^3J_{H-H}$ = 6.8 Hz) and 1.42 ($^3J_{H-H}$ = 6.8 Hz) ppm with an integration ratio of 6H each correspond to the methyl of *i*Pr, while the methine protons appear as a septet at δ 4.02 ppm with the same coupling constant. In the $^{13}C\{^1H\}$ NMR spectrum, the quaternary NCN occurs at δ 164.56 ppm, roughly 2 ppm upfield shifted than $[L(Cl)Si:]$ (Chart 4.3a). This observation is consistent with other amidosilylenes accessed by a similar pathway, namely, $[L(Me_2N)Si:]$ ^[16] and $[L\{(SiMe_3)_2N\}Si:]$ ^[17] (Chart 4.3b). The $^{29}Si\{^1H\}$ NMR displays two sharp signals in

the opposing phase for SiMe₃ (δ 3.48 ppm) and the silylene (δ 1.16 ppm). Although the silylene singlet is upfield shifted from its starting material (Chart 4.3a),^[14] it is the most downfield signal amongst the aforementioned amidosilylenes (Chart 4.3b).^[16,17]

Chart 4.3 Structures of (a) amidinato chlorosilylene; and (b) amidinato amidosilylenes. Their corresponding NCN and silylene chemical shifts, in $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR respectively, are given in ppm.

4.2.2 Synthesis of Amidinato Amidosilylene-Borane Adduct (4.13)

Treatment of amidinato amidosilylene **4.12** with $[\text{BH}_3 \cdot \text{THF}]$ in toluene furnished the silylene-borane adduct $[\text{L}\{(\text{SiMe}_3)(\text{Ar})\text{N}\}\text{Si}:\rightarrow\text{BH}_3]$ (**4.13**, Scheme 4.6). While the reaction proceeded at ambient temperature overnight, it should be noted that approximately two equivalents of borane was required for all silylene to be consumed. This suggests significant steric hindrance around the silylene lone pair electrons which could hamper coordination. Nevertheless, the product could be isolated in 69% yield and its structure was confirmed by single crystal XRD (Figure 4.2).

Scheme 4.6 Synthesis of silylene-borane **4.13**.

Figure 4.2 ORTEP drawing of **4.13** with thermal ellipsoids at 20% probability level. As there are two independent molecules in the asymmetric unit with slightly different bond lengths and angles, only one independent molecule is discussed here for clarity. For the same reason, selected hydrogen atoms are elided. Selected bond lengths (Å) and bond angles (°): Si1-B1 1.623(11), B1-H 0.98, Si1-N1 1.926(3), Si1-N2 1.898(2), Si1-N3 1.773(3); Si1-B1-H 109, H1BB-B1-H2BB 110, N1-Si-N2 68.1(1), N1-C5-N2 106.9(3), N2-Si1-N3 107.7(1), B1-Si1-N3 126.4(5), B1-Si1-N1 113.8(5).

Comprehensive multinuclear NMR analysis was also performed on **4.13**.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra stem from the amidinate and amido ligands. In ^{11}B coupled ^1H NMR spectroscopy, the BH_3 moiety appears as a quartet at δ - 44.05 ($^1J_{\text{B-H}} = 92.9$ Hz) ppm. The region of the signal is expected for four-coordinated boron species and coincides well with silylene-boranes discussed in Chapter 3 (Chart 4.4). Most noticeably, the well-defined silylene signal in **4.12** (δ 1.16 ppm) is now completely diminished and is attributable to considerable quadrupolar broadening prescribed by the adjacent boron atom. Likewise, the B- H resonances are shrouded in the ^1H NMR spectrum.

Chart 4.4 Structures and ^{11}B NMR signals (ppm) of silylene-boranes introduced in Chapter 3.

4.2.3 Synthesis of Amidinato Amidosilylene-Monotriflate Borane (4.14)

Treatment of **4.13** with equimolar methyl triflate [MeOTf] (OTf = OSO₂CF₃) in toluene at ambient temperature gave the corresponding monotriflate borane [L{(SiMe₃)(Ar)N}Si:→BH₂OTf] (**4.14**, Scheme 4.7). The air- and moisture-sensitive colourless crystals were collected from a saturated toluene solution in 73% yield.

Scheme 4.7 Synthesis of silylene-monotriflate borane **4.14**.

The solid state structure of **4.14** is verified by XRD as represented in Figure 4.3. The chiefly unique feature is the covalently-bound triflate group with a B1–O1 bond length of 1.601(5) Å. Although this is marginally elongated compared to its less sterically-hindered analogues (Chart 4.5), it still falls within the range of B–O single bonds. Both Si1 and B1 atoms adopt distorted tetrahedral geometries as before and the Si–B bond length in this case is 1.998(5) Å.

Figure 4.3 ORTEP drawing of **4.14** with thermal ellipsoids at 20% probability level. Selected hydrogen atoms and solvent molecules are elided for clarity. Selected bond lengths (Å) and bond angles (°): Si1-B1 1.998(5), B1-H1BB 1.15(4), B1-H2BB 1.09(4), B1-O1 1.601(5), Si1-N1 1.857(3), Si1-N2 1.835(3), Si1-N3 1.724(3); Si1-B1-H1BB 109(2), Si1-B1-H2BB 112(2), Si1-B1-O1 105.2(3), O1-B1-H2BB 110(2), N1-Si1-N2 71.4(1), N1-C5-N2 106.4(3), N1-Si1-N3 116.8(1), N3-Si1-B1 117.6(2), B1-Si1-N2 113.9(2).

Chart 4.5 Structures, B–O bond lengths (Å), $^{11}\text{B}\{^1\text{H}\}$ and ^{19}F NMR signals (ppm) of related monotriflate boranes.

Based on multinuclear NMR spectroscopy, the structure of **4.14** was also corroborated. Both amidinate and amido ligands are well-identified in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. A broad resonance is observed at δ -11.37 ppm in the $^{11}\text{B}\{^1\text{H}\}$ NMR, reminiscent of other amidosilylene monotriflate boranes (Chart 4.5).

The downfield shift from its borane starting material is also a trend prevalent amongst related compounds as established in Chapter 3. In ^{19}F NMR, the distinctive signal at δ -74.89 (s) ppm affirms the presence of an attached OTf. Likewise to its precursor, only the SiMe_3 group was detected in $^{29}\text{Si}\{^1\text{H}\}$ NMR (δ 9.60 ppm) and B–H resonances remain elusive in the ^1H NMR.

4.2.4 B–H Activation by Amidinato Amidosilylene-Monotriflate Borane (4.14)

While no signs of decomposition were uncovered upon heating a toluene solution of **4.13** at 120 °C overnight, as monitored by ^{11}B NMR, compound **4.14** underwent a B–H bond activation in refluxing toluene to afford amidinato borane [LB(H)Si(H)(OTf){N(SiMe₃)Ar}] (**4.15**, Scheme 4.8). **4.15** is a constitutional isomer of **4.14** and was isolated as colorless crystals from the reaction mixture in 90% yield.

Scheme 4.8 Synthesis of amidinato borane **4.15**.

According to its X-ray crystal structure (Figure 4.4), the amidinate ligand coordinates in a bidentate fashion to the boron atom, which assumes a distorted tetrahedral geometry. The nearly equal B–N(amidinate) bond lengths (1.569(9), 1.572(8) Å) are comparable with those of the amidinato borane [PhC(N*i*Pr)₂B(C₆F₅)₂] (Chart 4.6a),^[18] while the B1–Si1 bond length (2.033(7) Å) is akin to that of Lewis base-silylborane complexes (Chart 4.6b) such as [PyB(Br)₂Si*t*Bu₃]^[19] and [I*i*PrMeB(pin)SiPh₃] (I*i*PrMe = {MeCN*i*Pr}₂C:).^[20] Interestingly, of the two possible enantiomers arising from the chiral Si center, only the *S*-isomer is obtained from the reaction.

Figure 4.4 ORTEP drawing of **4.15** with thermal ellipsoids at 30% probability level. Selected hydrogen atoms and solvent molecules are elided for clarity. Selected bond lengths (Å) and bond angles (°): B1-Si1 2.033(7), B1-H1B 1.2(1), B1-N1 1.569(9), B1-N2 1.572(8), Si1-H1SI 1.4(2), Si1-O1 1.781(5), Si1-N3 1.722(5); Si1-B1-H1B 117(8), N1-B1-Si1 115.7(5), N2-B1-H1B 111(8), N1-B1-N2 82.2(5), N1-C5-N2 100.9(6), B1-Si1-O1 108.5(3), O1-Si1-N3 105.3(3), N3-Si1-H1SI 106(6), H1SI-Si1-B1 116(6).

Chart 4.6 Structures and bond lengths (Å) of related (a) amidinato borane; and (b) Lewis base-silylborane complexes.

In the ^1H NMR spectrum, the *i*Pr fragment appears as four doublets, each with an integration ratio of 3H, and two overlapping septets with a total integration ratio of 2H. Furthermore, the *t*Bu moieties on the amidinate backbone now splits into two singlets (δ 0.94 and 1.20 ppm). These data collectively suggest that, unlike in **4.12** to **4.14**, the high degree of steric hindrance instilled by the amido ligand has

resulted in chemical inequivalence due to limited rotation around the Si–N and Si–B bonds. Additionally, a broad resonance at δ 5.91 ppm is observed, corresponding to Si–H. This chemical shift agrees with other known silyltriflates (Chart 4.7a).^[21] It also exhibits a pair of satellites which revealed a $^1J_{\text{Si-H}}$ coupling constant of 200 Hz. The $^{11}\text{B}\{^1\text{H}\}$ NMR signal (δ -5.51 ppm) is upfield shifted in comparison with that of the amidinato boranes, such as $[\text{PhC}(\text{N}i\text{Pr})_2\text{B}(\text{C}_6\text{F}_5)_2]$ ^[18] and $[\text{PhC}(\text{NCy})_2\text{BCl}_2]$ (Chart 4.7b),^[22] but downfield shifted from its precursor (δ -11.37 ppm). Although the B–H resonance still evaded detection, its existence is certainly validated by the ^{11}B coupled ^1H NMR (δ -5.45 ppm, d, $^1J_{\text{B-H}} = 109.3$ Hz). The B–Si signal was located at δ 4.91 (br) ppm with the aid of the adjacent H which enabled a ^{29}Si INEPT NMR spectrum to be effectively acquired. The ^{19}F NMR signal at δ -76.55 ppm further corroborates the covalently-attached OTf moiety.

Chart 4.7 Structures of related (a) silyltriflates and their Si–H signals in ^1H NMR; and (b) amidinato boranes and their ^{11}B signals. All values are given in ppm.

The isomerization from **4.14** to **4.15** is postulated to proceed as outlined in Scheme 4.9. Firstly, the lone pair electrons on the imino nitrogen atom donates to the σ^* orbital of the B–H bond in **4.14**, while the B–H σ electrons synergistically donate back to the empty p orbital on the Si center. Plainly, the B–H bond of BH_2OTf undergoes an 1,1-oxidative addition on the Si(II) centre of the amidinato amidosilylene, along with the N_2CSi four-membered ring opening to generate **4.14A**. The Si–N(amidinate) σ bond in **4.14A** then attacks the boron center, along

with a 1,2-migration of the OTf group to the Si atom, to form **4.15**. This mechanism is substantiated by mechanistic and theoretical studies (see sections 4.2.6 and 4.2.7 respectively).

Scheme 4.9 Proposed mechanism for the isomerization of **4.14** to **4.15**.

4.2.5 Mechanistic Studies for the Formation of Amidinato Borane (4.15)

In order to ascertain the bridging chelation mode of the amidinate ligand suggested for **4.14A**, compound **4.15** was treated with 4-dimethylaminopyridine (DMAP) in refluxing toluene. We hypothesized that binding of a Lewis base to the boron center will provide sufficient driving force to alter the manner in which the amidinate coordinates. Indeed, the reaction led to the bridged silylboronium cation in $[(\mu-\kappa 1:\kappa 1-L)B(H)(DMAP)Si(H)\{N(Ar)SiMe_3\}]OTf$ (**4.16**, Scheme 4.10), whose structure is analogous to **4.14A** and justifies its plausibility. **4.16** was isolated as a colourless crystalline solid in 85% yield.

Scheme 4.10 Synthesis of bridged silylboronium salt **4.16** from **4.15**.

XRD studies established the (S_B, R_{Si})-diastereomer to be selectively produced (Figure 4.5). The solid state structure of **4.16** also features a separated ion pair with the B...O distance (7.186 Å) being longer than the sum of their van der Waal's radii (ca. 3.48 Å), indicating negligible interactions between said atoms. The amidinate ligand is $\mu-\kappa 1:\kappa 1$ -bridged between the boron and silicon centres; both B and Si adopt tetrahedral geometries. The C–N bond lengths are unequal (C5–N1: 1.365(4); C5–N2: 1.345(4) Å), but they are evocative of those exhibited by **4.14** (1.347(4), 1.342(4) Å). The Si–N(amidinate) bond length (1.818(3) Å) and B–N(amidinate) bond length (1.570(5) Å) are reminiscent of those in **4.14** (Si–N: 1.835(3), 1.857(3) Å) and **4.15** (B–N: 1.569(9), 1.572(8) Å) respectively, whereby

the amidinate ligand is bidentate coordinated to the central Si (**4.14**) and B (**4.15**) atoms. Moreover, the B–N(DMAP) bond length (B1–N3: 1.580(4) Å) is comparable with that of [(DMAP)₂B(Fl)]Br (1.582(5) Å, Fl = fluorene)^[23] and the B1–Si1 bond (1.998(3) Å) is shorter than that in its precursor (2.033(7) Å).

Figure 4.5 ORTEP drawing of **4.16** with thermal ellipsoids at 30% probability level. Selected hydrogen atoms and solvent molecules are elided for clarity. Selected bond lengths (Å) and bond angles (°): B1–Si1 1.998(3), B1–H1B 1.09(3), B1–N3 1.580(4), B1–N2 1.570(5), Si1–H1S 1.38(4), Si1–N1 1.818(3), Si1–N4 1.748(2), C5–N1 1.365(4), C5–N2 1.345(4); Si1–B1–N2 100.8(2), N2–B1–N3 109.0(2), N3–B1–H1B 108(2), H1B–B1–Si1 115(2), B1–Si1–N1 89.6(1), N1–Si1–N4 113.5(1), N4–Si1–H1S 107(1), H1S–Si1–B1 113(1), N1–C5–N2 119.1(3).

4.16 was also fully characterized by multinuclear NMR. Analogous to **4.15**, the ¹H NMR spectrum displays two singlets at δ 0.97 and 1.06 ppm for two inequivalent *t*Bu chemical environments of the amidinate ligand. The two septets due to the *i*Pr methine protons are now well separated (δ 3.52 and 3.61 ppm). Conversely, three of the doublets overlap in the region ca. δ 1.27 ppm (9H), while the last doublet occurs at δ 1.16 ppm (3H). The Si–H resonance (δ 5.02 ppm) is

upfield shifted and expectedly broad, with a coupling constant of 211 Hz calculated from the satellites. The ^{11}B NMR signal (δ -44.33 ppm, d, $J_{\text{B-H}} = 89.2$ Hz) is significantly upfield shifted alongside that of **4.15** (δ -11.37 ppm). However, a similar upfield shift was reported for the conversion of 9-bromo-9-borafluorene (δ 65.8 ppm) to its corresponding bis(DMAP)-boronium bromide $[(\text{DMAP})_2\text{B}(\text{FI})]\text{Br}$ (δ 4.6 ppm).^[23] The ^{29}Si INEPT NMR spectrum of **4.16** shows a broad signal at δ -0.52 ppm corresponding to the boron-coordinated Si atom. Most importantly, the sharp singlet in the ^{19}F NMR at δ -77.54 ppm indicates the presence of a free triflate group.

Scheme 4.11 Resonance interpretations of the cation in **4.16**.

On the basis of these X-ray crystallographic data and ^{11}B NMR signal, it can be surmised that the positive charge in the cation of **4.16** is delocalized between the boron and silicon centres (Scheme 4.11). This conclusion is ratified by topological analysis using QTAIM (Quantum Theory of Atoms in Molecules) calculations, which was performed to probe the nature of the B–Si bond in **4.16**. The electron density, $\rho(r)$, at the (3,-1) bond critical points (BCPs) of N–B (0.14) and N–Si (0.10) bonds, along with the correspondingly positive Laplacian ($\nabla^2\rho(r)$; +0.24 and +0.30), indicate a closed-shell interaction i.e., a donor-acceptor bond. This is further supported by the contour plot of the Laplacian distribution (Figure 4.6), showing charge concentration at the nitrogen end of the amidinate ligand

(solid lines) and charge depletion at the boron and silicon end (dotted lines), respectively. In contrast, the $\rho(r)$ at the BCPs of the B–Si (0.12) bond, along with the negative Laplacian (-0.19), indicate an open-shell interaction i.e., a covalent bond. Charge concentration in the middle of the B–Si bond, as depicted in the Laplacian distribution plot, confirms this statement.

Figure 4.6 Contour plot of Laplacian distribution [$\nabla^2\rho(r)$] in the N-B-Si plane and QTAIM of the cation in **4.16**. Solid lines indicate the areas of the charge concentration ($\nabla^2\rho(r) < 0$) while dotted lines mean the charge depletion ($\nabla^2\rho(r) > 0$). Brown, blue, orange dots denote (3,-3), (3,-1), (3,+1) critical points respectively. Solid lines connecting atomic nuclei (black) are the bond paths, and those lines (purple) separating the atomic basins indicate the zero-flux surface crossing the molecular plane.

4.2.6 Mechanistic Studies for the Formation of Silylboronium Salt (4.16)

To gain insight into the mechanism for the synthesis of **4.16**, we examined the reaction between **4.15** and DMAP by ^1H NMR spectroscopy (Figure 4.7). Upon addition of DMAP to a C_6D_6 solution of **4.15**, the latter disappeared rapidly even at room temperature. An immediate shift in the signals, most prominently of the Si–H and NMe_2 fragments, was identified. New singlets at δ 5.78 and 2.86 ppm with an integral ratio of 1:6 suggest the generation of an intermediate with similar Si–H environment as **4.15** ($\delta_{\text{Si-H}} = 5.91$ ppm) but with DMAP ($\delta_{\text{NMe}_2} = 2.23$ ppm) already coordinated. This intermediate is short-lived in solution at ambient temperature (ca. 30 min) and ultimately transforms into **4.16** over a period of 5 hours.

Figure 4.7 Reaction of **4.15** and DMAP as monitored by ^1H NMR spectroscopy.

Hence, we deduced the following mechanism for the formation of **4.16** from **4.15** (Scheme 4.12). Donation of lone pair electrons from the N donor of DMAP to

the boron centre in **4.15** occurs initially. As a consequence, one of the chelating N donors on the amidinate ligand is displaced, furnishing intermediate **4.15A**. The structure of **4.15A** is inferred from the NMR data collected for the species that forms immediately upon addition of DMAP to **4.15** (i.e. presence of an Si–H environment akin to **4.15** and coordinated DMAP molecule). Upon its fast generation, the imino nitrogen atom of the amidinate ligand on **4.15A** attacks the silicon centre, along with the displacement of the OTf group, to give **4.16**. Similar amidinate ring opening for small molecules activation was found in the reaction of $[\{HC(NR)_2\}B(C_6F_5)_2]$ ($R = iPr, tBu$) toward CO, $tBuNC$, $PhC(O)H$, etc..^[18]

Scheme 4.12 Proposed mechanism for the formation of **4.16** from **4.15**.

The striking resemblances between **4.16** and **4.14A** elicit the speculation that **4.16** can be generated directly from **4.14A** by a simple displacement of OTf with DMAP. As predicted, treatment of **4.14** with DMAP in refluxing toluene overnight afforded **4.16**. Tracking the reaction by 1H NMR spectroscopy revealed that the transformation from **4.14** to **4.16** proceeds without observation of **4.15** (Figure 4.8). When DMAP was introduced into a C_6D_6 solution of **4.14**, only small amounts of **4.16** and free DMAP were distinguished from the 1H NMR spectrum. After ca. 24 hours at 60 °C, **4.14** cleanly converts to **4.16**.

Figure 4.8 Reaction of **4.14** and DMAP as monitored by ^1H NMR spectroscopy.

These results point toward the consensus that the silylene moiety in **4.14** first undergoes B–H oxidative addition to generate **4.14A**, which is not detected experimentally. In the presence of DMAP, the boron center of **4.14A** is attacked by the Lewis base with a concomitant displacement of OTf to yield **4.16** (Scheme 4.13). Otherwise, the Si–N(amidinate) σ bond attacks the B to collapse the five-membered ring and a 1,2-OTf migration furnishes isomerized product **4.15** (Scheme 4.9).

Scheme 4.13 Proposed mechanism for the formation of **4.16** from **4.14**.

It is noteworthy that in an analogous reaction between $[L\{(SiMe_3)_2N\}Si:\rightarrow BH_2OTf]$ and DMAP mentioned in Chapter 3, only the corresponding bis(Lewis base) boronium salt was afforded by a formal displacement of the triflate group by DMAP (Scheme 4.14). No B–H activation is apparent in this situation, further highlighting the uniqueness and competency of amidinato amidosilylene **4.12**.

Scheme 4.14 Reaction of $[L\{(SiMe_3)_2N\}Si:\rightarrow BH_2OTf]$ and DMAP.

4.2.7 Theoretical Studies for the B–H Activation by Amidinato Amidosilylene-Monotriflate Borane (4.14)

In support of the experimental observations, DFT calculations were performed (M06-2X/Def2-TZVP//M06-2X/Def2-SVP). The reference point for the reaction profile (Figure 4.9) is the sum of the energy of **4.13**, MeOTf and DMAP at infinite separation.

Figure 4.9 Free energy profile for the reactions of **4.13** at 384 K; TS = transition state.

When **4.13** reacts with MeOTf (Scheme 4.7), thermodynamically stable monotriflate borane **4.14** ($\Delta G_{\text{4.13+MeOTf} \rightarrow \text{4.14}} = -43.9$ kcal/mol) is formed. Subsequently, the B–H bond of the BH₂OTf unit undergoes activation with the

[L{N(SiMe₃)Ar}Si:] moiety in **4.14** (Scheme 4.9) to afford intermediate **4.14A** ($\Delta G_{4.13+\text{MeOTf} \rightarrow 4.14\text{A}} = -40.1$ kcal/mol, Figure 4.10). This proceeds via **TS1** (Figure 4.11a) with a relatively high energy barrier ($\Delta G^\ddagger = 32.5$ kcal/mol), corroborating the hypothesis that the generation of **4.14A** is a slow process.

Figure 4.10 Optimized geometry of **4.14A**.

In the presence of DMAP, the displacement of OTf in **4.14A** occurs through **TS4** ($\Delta G^\ddagger = 35.7$ kcal/mol, Figure 4.11d) which exhibits the B atom interacting weakly with an incoming DMAP molecule (B1 $\cdots$ N4) and a leaving triflate group (B1 $\cdots$ O1). The eventual production of **4.16** is exergonic by -49.1 kcal/mol with respect to the reference starting materials. Contrarily, in the absence of DMAP, the isomerization of **4.14A** to **4.15** (Scheme 4.9), involving a 1,2-triflate migration and formation of an N(amidinate)–B bond, ensues with a significantly lower barrier of 5.5 kcal/mol via **TS2** (Figure 4.11b).

Figure 4.11 Optimized geometries of transition states.

Further reaction of **4.15** with DMAP progresses through **TS3** (Figure 4.11c). This transition state displays a weak interaction between the B atom and N donor of DMAP (B1...N3), while featuring an elongated Si–N(amidinate) bond (Si1...N1). Its structure is akin to that proposed for intermediate **4.15A**, substantiating its existence. Finally, displacement of OTf by chelation of the amidinate ligand gives **4.16**.

4.3 Conclusion

The activation of B–H bond in BH₂OTf can be achieved by amidinato amidosilylene [L{(SiMe₃)(Ar)N}Si:] (L = PhC(N*t*Bu)₂, Ar = 2,6-*i*PrC₆H₃) in monotriflate borane **4.14**. It proceeds through the synergic effort of the non-innocent amidinate ligand and low valent silicon centre to promote double electron transfer with the B–H bond. In other words, donation of electrons into the B–H σ^* orbital and simultaneous back donation of B–H σ electrons into the empty p orbital of the Si(II) center facilitates the formidable bond cleavage. As such, **4.14** can isomerize to amidinato borane **4.15** or, in the presence of an external Lewis base such as DMAP, form the bridged silylboronium salt **4.16**. Mechanistic and theoretical analyses collectively prove that intermediate **4.14A**, while not detectable experimentally, should be key to these transformations. Furthermore, the fact that reaction between an analogous amidinato amidosilylene-monotriflate borane and DMAP failed to furnish any B–H activated product emphasizes the exceptional properties of amidinato amidosilylene **4.12**.

4.4 Experimental

General Considerations: All manipulations, unless otherwise stated, were performed by using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon. Toluene and hexane were dried using an MBraun solvent purification system. Benzene- d_6 was dried and distilled over molten potassium. All NMR spectra were recorded on JEOL ECA 400 or Bruker 400 spectrometers. ^1H NMR spectra were referenced to residual solvent peaks. All chemicals were used as received, unless stated otherwise. $[\text{L}(\text{Cl})\text{Si}:]$ ($\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$)^[14] and $[\text{LiN}(\text{SiMe}_3)\text{Ar}]$ ($\text{Ar} = 2,6\text{-}i\text{PrC}_6\text{H}_3$)^[15] were synthesized according to literature procedures.

X-ray data collection and structural refinement: Intensity data for compounds **4.12** to **4.16** were collected by using a Bruker APEX II diffractometer. Reflections were measured at T / K (see section 4.5.1). The structures were solved by direct-phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2 .^[24] All nonhydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. A summary of selected crystallographic data is provided in the section 4.5.1.

Synthesis of 4.12: Toluene (ca. 40 mL) was added to a mixture of $[\text{L}(\text{Cl})\text{Si}:]$ (1.47 g, 5.00 mmol, 1.0 equiv) and $[\text{LiN}(\text{SiMe}_3)\text{Ar}]$ (1.28 g, 5.00 mmol, 1.0 equiv). The reaction mixture was allowed to stir at room temperature for 16 hours. Volatiles were removed under vacuum and the resulting residue was washed with hexane to afford the product as a yellowish powder. Colourless crystals of **4.12** were harvested from a saturated toluene solution stored at 0 °C for 3 days.

Yield: 4.66 g (92 %); M.p.: 60-65 °C.

^1H NMR (400.1 MHz, C_6D_6 , 25.9 °C): δ = 0.33 (s, 9H, SiMe_3), 1.29 (s, 18H, $t\text{Bu}$), 1.37 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, CHMe_2), 1.42 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, CHMe_2), 4.02 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 2H, CHMe_2), 6.87-7.10 (m, 5H, Ph), 7.19-7.26 (m, 2H, ArH), 7.32-7.35 (m, 1H, Ph) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6 , 27.0 °C): δ = 4.37 (SiMe_3), 24.73 (CHMe_2), 28.13 (CHMe_2), 33.33 (CMe_3), 54.61 (CMe_3), 124.77, 125.33, 127.64, 129.72, 131.89, 135.94, 145.37, 148.49 (Ph), 164.56 (NCN) ppm.

$^{29}\text{Si}\{^1\text{H}\}$ NMR (78.7 MHz, C_6D_6 , 26.9 °C): δ = 1.16 (LSiN), 3.48 (SiMe_3) ppm.

HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{50}\text{N}_3\text{Si}_2$: 508.3543 $[(M+H)]^+$; found: 508.3538.

Synthesis of 4.13: [$\text{BH}_3 \cdot \text{THF}$] (1.0 M in THF, 13.3 mL, 2.0 equiv.) was added to a solution of **4.12** (3.40 g, 6.69 mmol, 1.0 equiv.) in toluene (20 mL) at ambient temperature. The mixture was allowed to stir and solution changed from clear orange to cloudy yellow after 16 hours. Upon filtration and concentration, colourless crystals of **4.13** were obtained.

Yield: 2.37 g (69 %); M.p.: 200-203 °C.

^1H NMR (399.5 MHz, C_6D_6 , 25.6 °C): δ 0.27 (s, 9H, SiMe_3), 1.27 (s, 18H, $t\text{Bu}$), 1.29 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6H, CHMe_2), 1.54 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 6H, CHMe_2), 3.84 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 2H, CHMe_2), 6.83-6.99 (m, 3H, Ph), 7.11-7.15 (m, 2H, Ph), 7.18-7.25 (m, 3H, Ph) ppm, H_B signals were not detected.

$^{11}\text{B}\{^1\text{H}\}$ NMR (128.2 MHz, C_6D_6 , 25.9 °C): δ -44.30 (s) ppm.

^{11}B NMR (128.2 MHz, C_6D_6 , 25.9 °C): δ -44.05 (q, $^1J_{\text{B-H}} = 92.9$ Hz) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6 , 26.9 °C): δ 3.72 (SiMe_3), 25.34, 26.86 (CHMe_2), 28.31 (CHMe_2), 32.46 (CMe_3), 56.16 (CMe_3), 125.01, 126.27, 130.13, 130.65, 132.66, 142.58, 147.45 (Ph), 176.03 (NCN) ppm.

$^{29}\text{Si}\{^1\text{H}\}$ NMR (78.7 MHz, C_6D_6 , 26.6 °C): δ 6.66 (SiMe_3) ppm, Si_B signal was not detected.

HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{53}\text{BN}_3\text{Si}_2$: 522.3871 [$(M+H)^+$]; found: 522.3854.

Synthesis of 4.14: MeOTf (0.192 g, 0.13 mL, 1.17 mmol, 1.0 equiv.) was added to a solution of **4.13** (0.608 g, 1.17 mmol, 1.0 equiv.) in toluene (20 mL) at ambient temperature. The mixture was allowed to stir and solution changed from pale yellow to colourless after 16 hours with slight bubbling. Upon filtration and concentration, colourless crystals of **4.14** were

obtained.

Yield: 0.570 g (73 %); M.p.: 125-130 °C.

^1H NMR (395.9 MHz, C_6D_6 , 26.4 °C): δ 0.17 (s, 9H, SiMe_3), 1.17 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, CHMe_2), 1.21 (s, 18H, $t\text{Bu}$), 1.39 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, CHMe_2), 3.60 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 2H, CHMe_2), 6.87-7.13 (m, 7H, Ph), 7.67-7.69 (m, 1H, Ph) ppm, H_B signals were not detected.

$^{11}\text{B}\{^1\text{H}\}$ NMR (128.2 MHz, C_6D_6 , 26.0 °C): δ -11.37 (br) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6 , 26.4 °C): δ 3.44 (SiMe_3), 25.58, 26.63 (CHMe_2), 28.39, 32.25 (CMe_3), 56.54 (CMe_3), 125.46, 127.11, 127.91, 129.45, 130.26, 130.99, 131.32, 139.84, 146.47, 147.01 (Ph), 178.40 (NCN) ppm, C_F signal was not detected.

^{19}F NMR (372.5 MHz, C_6D_6 , 26.6 °C): δ -74.89 (s) ppm.

$^{29}\text{Si}\{^1\text{H}\}$ NMR (78.7 MHz, C_6D_6 , 26.4 °C): δ 9.60 (SiMe_3) ppm, Si_B signal was not detected.

HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{52}\text{BF}_3\text{N}_3\text{O}_3\text{SSi}_2$: 670.3313 [$(M+H)$] $^+$; found: 670.3323.

Synthesis of 4.15: **4.14** (0.669 g, 1.00 mmol) was stirred overnight in refluxing toluene (20 mL). Upon cooling, filtration, and concentration, colourless crystals of **4.15** were obtained.

Yield: 0.601 g (90 %); M.p.: 146-151 °C.

^1H NMR (395.9 MHz, C_6D_6 , 24.9 °C): δ = 0.37 (s, 9H, SiMe_3), 0.94 (s, 9H, CMe_3), 1.20 (s, 9H, CMe_3), 1.24 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, CHMe_2), 1.27 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, CHMe_2), 1.48 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, CHMe_2), 1.58 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, CHMe_2), 3.68-3.77 (m, 2H, CHMe_2), 5.91 (br s, 1H, SiH), 6.79-7.15 (m, 7H, Ph), 7.95 (br, 1H, Ph) ppm, H_B signal was not detected.

$^{11}\text{B}\{^1\text{H}\}$ NMR (127.0 MHz, C_6D_6 , 25.3 °C): δ -5.51 (s) ppm.

^{11}B NMR (127.0 MHz, C_6D_6 , 25.2 °C): δ -5.45 (d, $^1J_{\text{B-H}} = 109.3$ Hz) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, C_6D_6 , 23.8 °C): δ 2.76 (SiMe_3), 25.05, 25.53, 25.99, 26.73 (CHMe_2), 28.46, 26.64 (CHMe_2), 30.52, 31.37 (CMe_3), 53.20, 53.37 (CMe_3), 115.74, 115.95, 124.73, 125.22, 126.44, 130.45, 133.24, 140.73, 147.28, 147.44 (Ph), 167.63 (NCN) ppm, C_F signal was not detected.

^{19}F NMR (372.5 MHz, C_6D_6 , 25.0 °C): δ -76.55 (s) ppm.

^{29}Si INEPT NMR (100.5 MHz, C_6D_6 , 23.8 °C): δ 4.91 (br, SiB), 9.72 (SiMe_3) ppm.

HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{52}\text{BF}_3\text{N}_3\text{O}_3\text{SSi}_2$: 670.3313 [$(M+H)$] $^+$; found: 670.3304.

Synthesis of **4.16**:

Method A: Toluene (20 mL) was added to a mixture of **4.14** (0.669 g, 1.00 mmol, 1.0 equiv.) and DMAP (0.122 g, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux overnight. Upon cooling, filtration, and concentration, colourless crystals of **4.16** were obtained.

Method B: Toluene (20 mL) was added to a mixture of **4.15** (0.669 g, 1.00 mmol, 1.0 equiv.) and DMAP (0.122 g, 1.00 mmol, 1.0 equiv.). The reaction mixture was heated under reflux overnight. Upon cooling, filtration, and concentration, colourless crystals of **4.16** were obtained.

Yield: 0.670 g (85 %); M.p.: 131-135 °C.

^1H NMR (399.5 MHz, C_6D_6 , 23.5 °C): δ 0.34 (s, 9H, SiMe_3), 0.97 (s, 9H, CMe_3), 1.06 (s, 9H, CMe_3), 1.16 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 3H, CHMe_2), 1.21-1.27 (m, 9H, CHMe_2), 2.39 (s, 6H, NMe_2), 3.52 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 1H, CHMe_2), 3.61 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 1H, CHMe_2), 5.02 (br s, 1H, SiH), 6.92-7.10 (m, 7H, Ph), 7.18-7.21 (m, 1H, Ph), 7.57-7.61 (m, 1H, Ph), 8.01-8.03 (m, 2H, Ph), 8.98-9.00 (m, 1H, Ph) ppm, H_B signal was not detected.

$^{11}\text{B}\{^1\text{H}\}$ NMR (128.2 MHz, C_6D_6 , 23.7 °C): δ -44.30 (s) ppm.

^{11}B NMR (128.2 MHz, C_6D_6 , 23.7 °C): δ = -44.33 (d, $^1J_{\text{B-H}} = 89.2$ Hz) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, C_6D_6 , 23.8 °C): δ = 4.30 (SiMe_3), 25.91, 25.97, 26.01, 26.35 (CHMe_2), 28.38, 29.06 (CHMe_2), 33.40, 33.63 (CMe_3), 39.25 (NMe_2), 60.23, 63.25 (CMe_3), 109.59, 125.00, 125.30, 126.12, 126.66, 129.25, 130.36, 131.54, 133.97, 134.14, 143.46, 144.00, 146.47, 146.85, 156.23 (Ph), 182.34 (NCN) ppm, C_F signal was not detected.

^{19}F NMR (375.9 MHz, C_6D_6 , 23.6 °C): δ = -77.54 (s) ppm.

^{29}Si INEPT NMR (78.7 MHz, C_6D_6 , 23.8 °C): δ = -0.52 (br, SiB), 8.45 (SiMe_3) ppm.

HRMS (ESI): m/z calcd for $\text{C}_{37}\text{H}_{61}\text{BN}_5\text{Si}_2$: 642.4559 [(M-OTf)] $^+$; found: 642.4572.

4.5 Appendices

4.5.1. Crystallographic Data

Compound	4.12	4.13	4.14	4.15	4.16
Formula	C _{31.75} H ₅₁ N ₃ Si ₂	C ₃₆₀ H ₆₀₃ B ₅ N ₃₆ Si ₂₄	C ₃₁ H ₅₁ BF ₃ N ₃ O ₃ SSi ₂	C ₃₄ H _{53.50} BF _{3.50} N ₃ O ₃ SSi ₂	C ₃₈ H ₆₁ BF ₃ N ₅ O ₃ SSi ₂
<i>M</i>	530.93	6163.96	669.79	717.84	791.96
<i>T</i> / K	100(2)	153(2)	153(2)	103(2)	103(2)
Color	Colourless	Colourless	Colourless	Colourless	Colourless
Crystal size / mm	0.140 × 0.200 × 0.220	0.180 × 0.220 × 0.260	0.180 × 0.220 × 0.300	0.200 × 0.300 × 0.400	0.060 × 0.160 × 0.320
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Orthorhombic
Space Group	<i>P</i> 1 21/ <i>n</i> 1	<i>P</i> <i>n</i> <i>m</i> <i>a</i>	<i>C</i> 1 <i>c</i> 1	<i>P</i> -1	<i>P</i> 21 21 21
<i>a</i> / Å	10.0242(3)	18.7999(15)	12.389(2)	9.3892(10)	9.98650(10)
<i>b</i> / Å	39.5342(11)	49.059(4)	14.859(3)	9.7169(15)	16.7242(2)
<i>c</i> / Å	16.8348(4)	10.4230(8)	20.791(4)	23.995(3)	25.8787(4)
<i>α</i> / °	90	90	90	96.495(8)	90
<i>β</i> / °	102.6294(12)	90	101.896(3)	96.455(5)	90
<i>γ</i> / °	90	90	90	113.821(10)	90
<i>V</i> / Å ³	6510.2(3)	9613.2(13)	3745.2(11)	1959.5(5)	4322.16(9)
<i>Z</i>	8	1	4	2	4
<i>d</i> _{calcd} / g cm ⁻³	1.083	1.065	1.188	1.217	1.217
<i>μ</i> / mm ⁻¹	0.132	0.132	0.198	0.196	1.636
<i>F</i> (000)	2324	3376	1432	766	1696
Index Ranges	-13 ≤ <i>h</i> ≤ 12	-23 ≤ <i>h</i> ≤ 23	-16 ≤ <i>h</i> ≤ 16	-11 ≤ <i>h</i> ≤ 11	-10 ≤ <i>h</i> ≤ 11
	-52 ≤ <i>k</i> ≤ 53	-61 ≤ <i>k</i> ≤ 51	-19 ≤ <i>k</i> ≤ 19	-12 ≤ <i>k</i> ≤ 12	-19 ≤ <i>k</i> ≤ 19
	-16 ≤ <i>l</i> ≤ 22	-13 ≤ <i>l</i> ≤ 12	-27 ≤ <i>l</i> ≤ 26	-30 ≤ <i>l</i> ≤ 30	-28 ≤ <i>l</i> ≤ 30
Reflections collected	67807	60074	26311	38434	22323
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2(<i>σ</i>)]	0.0637, 0.1327	0.0706, 0.1747	0.0467, 0.1038	0.1062, 0.2823	0.0393, 0.0952
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1163, 0.1613	0.1170, 0.2032	0.0646, 0.1145	0.1258, 0.3029	0.0423, 0.0987
Goodness-of-fit on <i>F</i> ²	1.026	1.028	1.074	1.034	1.038
Data / restraints / parameters	16788 / 129 / 709	9906 / 177 / 529	7368 / 2 / 416	8086 / 363 / 426	7561 / 0 / 501
Largest diff. peak and hole/ e Å ⁻³	0.971, -0.582	0.458, -0.490	0.352, -0.299	0.812, -0.772	0.376, -0.384

4.5.2. NMR Spectra of New Compounds

4.12: ^1H , ^{13}C , ^{29}Si

4.13: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{11}B , ^{13}C , ^{29}Si

4.14: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{13}C , ^{19}F , ^{29}Si

4.15: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{11}B , ^{13}C , ^{19}F , ^{29}Si INEPT

4.16: ^1H , $^{11}\text{B}\{^1\text{H}\}$, ^{11}B , ^{13}C , ^{19}F , ^{29}Si INEPT

4.5.3. Theoretical Calculations

Methods: In this present work, the geometry optimizations were carried out with M06-2X functional in the Def2-SVP basis set. The geometry optimizations were performed with the analytically constructed energy gradient as implemented in the Gaussian program package.^[25] In the optimized M06-2X/Def2-SVP geometries, the harmonic vibrational frequency calculations were performed with the analytical force-constant matrix to verify the nature of the stationary points. That is, the local minimum (no imaginary frequencies) and the transition state (one imaginary frequency). In the same optimized geometries, higher-level single-point energy calculations were also performed, using the Def2-TZVP basis set. The relative energies in the reaction profile are based on the differences of the free energies (ΔG ; kcal mol⁻¹) at M06-2X/Def2-TZVP//M06-2X/Def2-SVP level of theory. The wave function file generated from the quantum code was used to perform QTAIM^{[26],[27]} analysis in the MultiWfn^[28] program suite.

Table S4.1 Geometrical coordinates of **4.13**.

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
5	0.372934	-0.018821	-2.868328
1	0.941250	-1.072011	-3.126305
1	1.037167	0.960503	-3.171770
6	-1.832423	2.481636	-0.614881
6	-2.849204	2.989020	0.414930
1	-3.839410	2.531910	0.295993
1	-2.966123	4.074194	0.280676
1	-2.496295	2.811403	1.441548
6	-2.403529	2.597026	-2.034244
1	-1.679851	2.215111	-2.768824
1	-2.625477	3.649848	-2.262926
1	-3.337872	2.027857	-2.131241
6	-0.573965	3.338830	-0.530501
1	-0.151316	3.314176	0.483445
1	-0.812542	4.380867	-0.785485
1	0.177543	2.975975	-1.245222
6	-2.169863	0.003647	-0.236584
6	-3.628428	0.001592	0.070634
6	-3.989792	-0.030413	1.421790
1	-3.210086	-0.062204	2.186659
6	-5.334037	-0.022371	1.782222
1	-5.613174	-0.045973	2.836391
6	-6.320487	0.014963	0.795948
1	-7.374303	0.020991	1.078056
6	-5.960136	0.044395	-0.550395
1	-6.729768	0.073477	-1.322737
6	-4.614508	0.038247	-0.917029

1	-4.333488	0.061364	-1.970873
6	-1.831382	-2.461708	-0.658157
6	-2.837699	-3.004305	0.364039
1	-2.477047	-2.859392	1.393051
1	-2.956182	-4.084583	0.196104
1	-3.828847	-2.543775	0.267247
6	-2.424963	-2.516955	-2.071845
1	-3.350699	-1.929150	-2.134122
1	-2.669293	-3.557065	-2.333729
1	-1.704622	-2.122515	-2.802889
6	-0.578303	-3.331231	-0.631347
1	0.166413	-2.940419	-1.338942
1	-0.832167	-4.356460	-0.934798
1	-0.141948	-3.363548	0.376733
6	0.055435	1.411241	2.646125

Table S4.2 Geometrical coordinates of MeOTf.

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
1	2.917527	-0.591691	0.596751
1	1.659309	-1.874360	0.541761
6	-1.113543	-0.350911	-0.001494
9	-2.047403	0.214590	0.733803
9	-0.835212	-1.550344	0.486744
9	-1.532315	-0.471389	-1.242006
8	1.379829	-0.271589	-0.772980
8	0.155803	1.849404	-0.743069
8	0.832821	0.733891	1.431873
16	0.412452	0.688624	0.055203
6	2.246240	-1.163885	-0.053596
1	2.814478	-1.692522	-0.824676

Table S4.3 Geometrical coordinates of **4.14**.

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
5	-0.014125	-1.972939	0.179431
1	-0.433620	-2.589621	-0.783803
1	-0.456929	-2.397003	1.231677
6	1.127440	1.095538	2.451004
6	1.617280	2.483762	2.880037
1	2.578497	2.751447	2.424094
1	1.756047	2.480928	3.970667
1	0.877700	3.260358	2.634600
6	2.236692	0.054409	2.639964
1	1.888262	-0.944346	2.344297

1	2.541573	0.027141	3.696392
1	3.123964	0.301322	2.041106
6	-0.060249	0.696369	3.319927
1	-0.867287	1.438955	3.250370
1	0.256308	0.621629	4.369421
1	-0.441223	-0.286926	3.010052
6	1.315511	1.429969	-0.052993
6	2.533834	2.285245	-0.087887
6	2.336544	3.668045	-0.166671
1	1.319985	4.066064	-0.210461
6	3.433096	4.524672	-0.189759
1	3.278803	5.602597	-0.250479
6	4.726295	4.002130	-0.134683
1	5.586358	4.672875	-0.151877
6	4.920285	2.623871	-0.058706
1	5.930174	2.214117	-0.017918
6	3.825939	1.759416	-0.034896
1	3.977349	0.681146	0.019614
6	1.160435	0.839574	-2.508145
6	1.613424	2.188185	-3.080477
1	0.848245	2.964839	-2.934529
1	1.772257	2.069238	-4.161848
1	2.558455	2.534496	-2.643605
6	2.309705	-0.171265	-2.566875
1	3.172934	0.172230	-1.982416
1	2.638893	-0.290548	-3.609487
1	2.000157	-1.155530	-2.190570
6	0.004445	0.306398	-3.346776
1	-0.352048	-0.650069	-2.938846
1	0.348500	0.124322	-4.374179
1	-0.827056	1.024277	-3.379969
6	-2.065449	3.182917	1.309443
1	-2.466945	2.805459	2.262775
1	-2.382147	4.231717	1.200542
1	-0.967181	3.156549	1.363241
6	-2.098545	2.948840	-1.733754
1	-1.002987	2.890790	-1.806016
1	-2.394875	4.008407	-1.774015
1	-2.530470	2.441603	-2.610387
6	-4.578933	2.165048	-0.118926
1	-4.995089	1.579925	-0.950545
1	-4.941023	3.201187	-0.206599
1	-4.979187	1.735619	0.809279
6	-3.171881	-0.528477	0.041328
6	-3.699501	-1.068745	-1.154480
6	-3.160070	-0.708253	-2.525335
1	-2.341852	0.002521	-2.371755
6	-2.594010	-1.941061	-3.237448
1	-1.827966	-2.437571	-2.624827

1	-2.144356	-1.659075	-4.201770
1	-3.388029	-2.675512	-3.441813
6	-4.207584	-0.015692	-3.403104
1	-5.055549	-0.684782	-3.615064
1	-3.763294	0.274743	-4.367767
1	-4.607216	0.891244	-2.926856
6	-4.767154	-1.968563	-1.086043
1	-5.169307	-2.383496	-2.013121
6	-5.326661	-2.338291	0.129440
1	-6.162092	-3.038845	0.164134
6	-4.807381	-1.803153	1.300685
1	-5.241277	-2.089097	2.261433
6	-3.739487	-0.901173	1.281849
6	-3.234475	-0.370629	2.610867
1	-2.412654	0.318210	2.389531
6	-4.301312	0.415501	3.379871
1	-4.671484	1.276921	2.806447
1	-3.885288	0.793247	4.326597
1	-5.165569	-0.220234	3.626336
6	-2.686254	-1.507985	3.479931
1	-3.491194	-2.200330	3.769667
1	-2.240910	-1.109079	4.404286
1	-1.922643	-2.087467	2.942227
6	3.960517	-2.684855	0.333836
9	4.848429	-3.613241	0.036804
9	4.014712	-2.431663	1.630929
9	4.274739	-1.569758	-0.324110
7	0.651308	1.072997	1.046365
7	0.659442	0.960157	-1.115246
7	-2.123797	0.477748	-0.013277
8	1.536175	-1.953823	0.193869
8	2.349325	-3.494329	-1.579338
8	1.953278	-4.348380	0.748236
16	2.282195	-3.272342	-0.152389
14	-0.463985	-0.033064	0.016136
14	-2.704945	2.166132	-0.136435

Table S4.4 Geometrical coordinates of **TS1**.

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
5	0.810479	-1.382173	0.332858
1	0.863576	-1.764011	1.464605
6	-0.392064	2.300510	-1.928821
6	-1.233894	3.433841	-1.332655
1	-2.049141	3.020271	-0.724996
1	-1.678763	4.026692	-2.145994
1	-0.640228	4.114154	-0.711842
6	-1.326900	1.476666	-2.826244

1	-0.774411	0.715084	-3.392347
1	-1.806236	2.161874	-3.538662
1	-2.125189	0.980095	-2.259175
6	0.682062	2.876893	-2.869721
1	1.150196	3.784704	-2.477661
1	0.208925	3.141472	-3.825960
1	1.459841	2.126304	-3.075868
6	1.369060	1.723517	-0.169539
6	1.831678	3.157147	-0.110622
6	2.942922	3.595587	-0.835883
1	3.408168	2.928441	-1.562780
6	3.445221	4.881088	-0.648199
1	4.310514	5.213145	-1.223767
6	2.845070	5.738792	0.274320
1	3.243070	6.743274	0.425599
6	1.736421	5.307762	1.001604
1	1.266905	5.970875	1.729451
6	1.234119	4.021886	0.809389
1	0.384528	3.672663	1.400606
6	3.213462	0.911555	1.311715
6	3.307280	2.129450	2.248215
1	4.096626	1.935487	2.988839
1	2.363479	2.274856	2.795322
1	3.560919	3.062356	1.731087
6	4.444134	0.852585	0.394568
1	4.609817	1.810916	-0.113889
1	4.316910	0.067983	-0.363672
1	5.343044	0.620841	0.984992
6	3.211269	-0.338674	2.201995
1	4.106056	-0.354174	2.840420
1	3.206944	-1.255359	1.600256
1	2.320264	-0.347814	2.846794
6	-3.186331	-0.871020	-0.080178
6	-3.148345	-2.263076	0.187384
6	-2.017485	-2.917498	0.967241
1	-1.429561	-2.113075	1.433369
6	-2.525861	-3.817195	2.099327
1	-3.251547	-3.298814	2.741437
1	-1.681667	-4.147207	2.722563
1	-3.013625	-4.720822	1.704796
6	-1.090204	-3.727914	0.051906
1	-1.631862	-4.583052	-0.381089
1	-0.237088	-4.131207	0.620232
1	-0.709485	-3.138429	-0.795048
6	-4.193522	-3.074480	-0.263304
1	-4.153527	-4.148965	-0.072844
6	-5.286728	-2.542977	-0.936093
1	-6.093604	-3.192525	-1.278284
6	-5.346870	-1.172377	-1.149911

1	-6.216896	-0.744132	-1.652447
6	-4.316979	-0.322901	-0.732402
6	-4.491216	1.170638	-0.949026
1	-3.529942	1.644559	-0.711876
6	-5.549798	1.736966	0.005977
1	-6.534537	1.291614	-0.204530
1	-5.638756	2.828316	-0.111961
1	-5.308672	1.523823	1.056912
6	-4.857829	1.522209	-2.395029
1	-4.181538	1.043212	-3.115829
1	-4.812019	2.611687	-2.546093
1	-5.882904	1.201527	-2.634702
6	-3.588793	-0.121563	2.890253
1	-4.551231	-0.107364	2.359128
1	-3.724125	0.354146	3.873496
1	-3.318148	-1.174927	3.053398
6	-2.576871	2.602699	1.879151
1	-1.705980	3.156916	1.501324
1	-2.778124	2.950364	2.905017
1	-3.442164	2.870460	1.257303
6	-0.601060	0.542269	2.855044
1	-0.396475	-0.516751	3.072862
1	-0.653447	1.082811	3.813401
1	0.258983	0.939479	2.292703
7	0.193548	1.404232	-0.863505
7	1.996323	0.814994	0.483454
7	-2.102212	-0.016674	0.335263
14	-0.558727	-0.195498	-0.512060
1	-0.924622	-0.932120	-1.810441
14	-2.229209	0.749641	1.934829
8	1.634099	-2.038777	-0.614315
16	2.382781	-3.422772	-0.351046
8	2.487197	-3.713721	1.056365
8	1.894025	-4.382306	-1.302220
6	4.072903	-2.945350	-0.945297
9	4.711890	-4.053260	-1.260201
9	4.733029	-2.317800	0.009742
9	3.986820	-2.164947	-2.003604

Table S4.5 Geometrical coordinates of **4.14A**.

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
5	-1.110451	0.772304	0.431907
1	-0.981757	1.382853	1.458561
6	0.408947	-2.414277	-1.834309
6	1.295174	-3.454265	-1.145652
1	2.059226	-2.955644	-0.536979
1	1.802039	-4.064230	-1.908269

1	0.717276	-4.132369	-0.505485
6	1.296140	-1.600638	-2.785746
1	0.703672	-0.874311	-3.359303
1	1.781495	-2.289601	-3.490170
1	2.088300	-1.061911	-2.249359
6	-0.635783	-3.114670	-2.717608
1	-1.087472	-3.990680	-2.240921
1	-0.130727	-3.464134	-3.628972
1	-1.429560	-2.417212	-3.022293
6	-1.310413	-1.621477	-0.121513
6	-1.925792	-2.986343	-0.063594
6	-3.045874	-3.333419	-0.821258
1	-3.466556	-2.617130	-1.527277
6	-3.606283	-4.602128	-0.695293
1	-4.480076	-4.869416	-1.290969
6	-3.049439	-5.529311	0.186599
1	-3.493521	-6.520576	0.288790
6	-1.922922	-5.189212	0.934998
1	-1.485469	-5.909936	1.626962
6	-1.361261	-3.920784	0.807386
1	-0.493737	-3.639204	1.408308
6	-3.115446	-0.683282	1.393622
6	-3.231332	-1.913249	2.311967
1	-4.007240	-1.701166	3.060419
1	-2.290257	-2.094016	2.852493
1	-3.526694	-2.830913	1.792607
6	-4.320931	-0.608427	0.443455
1	-4.535371	-1.577783	-0.020309
1	-4.149155	0.134559	-0.345249
1	-5.214972	-0.309267	1.009106
6	-3.167896	0.540203	2.322165
1	-4.105997	0.486922	2.890355
1	-3.156132	1.491712	1.780681
1	-2.330333	0.535518	3.032760
6	3.201551	0.873231	-0.107127
6	3.151524	2.264926	0.157631
6	2.014186	2.909200	0.938101
1	1.452052	2.109151	1.443480
6	2.513004	3.870112	2.022648
1	3.273548	3.407349	2.667790
1	1.669348	4.189778	2.651346
1	2.953256	4.778019	1.584393
6	1.043879	3.645114	0.008281
1	1.560378	4.467144	-0.512148
1	0.205065	4.069784	0.577650
1	0.626739	2.993411	-0.772248
6	4.181781	3.083163	-0.314437
1	4.135767	4.157859	-0.128245
6	5.266656	2.557960	-1.006133

1	6.061413	3.213661	-1.364711
6	5.334599	1.187830	-1.220969
1	6.198271	0.766560	-1.740196
6	4.320199	0.330838	-0.781169
6	4.500353	-1.161954	-0.995915
1	3.548252	-1.642285	-0.736153
6	5.582465	-1.716464	-0.060953
1	6.559932	-1.267894	-0.296538
1	5.674399	-2.808387	-0.171698
1	5.362482	-1.494826	0.992929
6	4.836094	-1.515625	-2.448756
1	4.137204	-1.046712	-3.154868
1	4.800090	-2.606192	-2.595415
1	5.850875	-1.183437	-2.714858
6	3.689262	0.223577	2.849005
1	4.634249	0.202595	2.287413
1	3.859529	-0.222963	3.840544
1	3.414072	1.279071	2.989048
6	2.683336	-2.539801	1.968962
1	1.804221	-3.128983	1.670148
1	2.942117	-2.830848	2.999652
1	3.521674	-2.826846	1.319339
6	0.717894	-0.496349	2.952916
1	0.467669	0.561064	3.120340
1	0.854395	-0.980491	3.932942
1	-0.147972	-0.967525	2.462462
7	-0.174348	-1.443732	-0.836802
7	-1.828660	-0.622178	0.590247
7	2.127866	0.019836	0.343375
14	0.578476	0.214563	-0.486034
1	0.900014	0.874843	-1.771467
14	2.307923	-0.688396	1.965357
8	-2.003742	1.546533	-0.564701
16	-2.321116	3.064051	-0.518773
8	-2.248376	3.608753	0.820219
8	-1.728443	3.756541	-1.636437
6	-4.121423	2.968409	-0.918339
9	-4.558658	4.179594	-1.204095
9	-4.802501	2.498444	0.116107
9	-4.326456	2.175621	-1.957600

Table S4.6 Geometrical coordinates of **TS2**.

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
5	0.571449	-1.423574	-0.106160
1	0.013875	-2.434834	0.250418
6	1.693843	-0.934633	2.427026
6	1.741929	-2.404985	2.862498

1	0.868026	-2.952397	2.481216
1	1.746978	-2.475703	3.960188
1	2.656102	-2.887974	2.482751
6	2.907459	-0.183519	2.982307
1	3.850587	-0.703281	2.764415
1	2.803827	-0.119159	4.075357
1	2.947784	0.834466	2.571801
6	0.415190	-0.272670	2.929662
1	0.414487	0.783111	2.629476
1	0.349438	-0.341237	4.025088
1	-0.475065	-0.761679	2.498333
6	2.566015	-1.095099	0.039992
6	4.032552	-0.897683	0.153004
6	4.865203	-1.999861	0.368819
1	4.437092	-3.004125	0.400830
6	6.232797	-1.809049	0.553549
1	6.883174	-2.666675	0.730941
6	6.765641	-0.520223	0.517448
1	7.836405	-0.370244	0.664030
6	5.932695	0.576974	0.296916
1	6.349907	1.584431	0.271397
6	4.562405	0.396977	0.118797
1	3.893023	1.243436	-0.042347
6	2.158607	-1.793964	-2.394142
6	3.191017	-2.921437	-2.520635
1	4.169585	-2.603781	-2.135260
1	3.316989	-3.195949	-3.577981
1	2.861023	-3.811059	-1.963978
6	2.675108	-0.524347	-3.076130
1	1.949198	0.293378	-2.978664
1	2.866612	-0.724371	-4.140929
1	3.613831	-0.189650	-2.610913
6	0.850371	-2.246409	-3.048474
1	0.423698	-3.108996	-2.514209
1	1.031540	-2.535170	-4.092998
1	0.108278	-1.431431	-3.064671
6	-2.861317	-0.820751	0.595084
6	-2.922812	-2.233293	0.647407
6	-2.631343	-3.095563	-0.572233
1	-1.903124	-2.561074	-1.199830
6	-2.025641	-4.456766	-0.229542
1	-1.161269	-4.358100	0.441988
1	-1.693841	-4.961009	-1.149066
1	-2.762150	-5.117458	0.251999
6	-3.904986	-3.278890	-1.404891
1	-4.666702	-3.818142	-0.820840
1	-3.696036	-3.857520	-2.317648
1	-4.336748	-2.313299	-1.698523
6	-3.319128	-2.835067	1.845038

1	-3.364801	-3.922789	1.908407
6	-3.660993	-2.073260	2.958876
1	-3.969846	-2.564976	3.882580
6	-3.603759	-0.687301	2.889356
1	-3.870610	-0.091353	3.764307
6	-3.197005	-0.036277	1.719817
6	-3.159634	1.482877	1.685187
1	-2.594941	1.784337	0.794530
6	-4.577021	2.061109	1.597975
1	-5.127504	1.684671	0.725106
1	-4.539708	3.159448	1.534123
1	-5.159084	1.795535	2.494489
6	-2.415414	2.078488	2.878779
1	-2.936342	1.892025	3.830571
1	-2.331016	3.167824	2.753096
1	-1.400902	1.668749	2.935220
6	-3.114804	-0.059212	-3.488641
1	-2.128676	0.291285	-3.826255
1	-3.858057	0.290785	-4.222231
1	-3.118528	-1.160137	-3.503054
6	-5.317386	0.080893	-1.352547
1	-5.381031	-0.435609	-0.383070
1	-5.721339	-0.591956	-2.122913
1	-5.969152	0.965944	-1.309163
6	-3.336075	2.454666	-1.755904
1	-3.759875	2.904293	-0.847213
1	-3.843185	2.901278	-2.625311
1	-2.271467	2.729534	-1.803428
6	0.876806	3.973691	-0.624842
9	0.042095	3.859059	-1.654078
9	2.018301	4.478514	-1.062293
9	0.346593	4.803820	0.256322
7	1.632803	-0.873063	0.960705
7	1.852215	-1.548189	-0.983613
7	-2.411222	-0.168220	-0.608937
8	-0.232693	1.934149	0.530284
8	1.658665	1.509826	-0.991223
8	2.073620	2.555869	1.234592
16	1.160842	2.318895	0.129696
14	-0.726200	-0.045306	-0.851758
1	-0.541443	0.740600	-2.090386
14	-3.555076	0.593454	-1.780337

Table S4.7 Geometrical coordinates of **4.15**.

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
5	0.761482	-1.354426	-0.267773
1	0.323776	-2.463902	-0.046648

6	1.716760	-0.941133	2.307474
6	2.036578	-2.396937	2.668367
1	1.309851	-3.078013	2.202203
1	1.997311	-2.536774	3.758762
1	3.047329	-2.666946	2.325251
6	2.726298	-0.001286	2.972764
1	3.763681	-0.292967	2.757391
1	2.585227	-0.042738	4.062639
1	2.565320	1.033232	2.639883
6	0.301544	-0.590850	2.763841
1	0.059769	0.443439	2.482721
1	0.213789	-0.688914	3.855292
1	-0.437104	-1.264544	2.299992
6	2.719799	-0.900257	-0.035204
6	4.160917	-0.609216	0.179460
6	5.065957	-1.659254	0.367172
1	4.715088	-2.691748	0.310379
6	6.405883	-1.382401	0.630016
1	7.110600	-2.200921	0.782450
6	6.843175	-0.059445	0.700285
1	7.892696	0.156307	0.906630
6	5.940911	0.986523	0.507671
1	6.283129	2.020817	0.562403
6	4.597603	0.717553	0.252269
1	3.875055	1.521736	0.108767
6	2.480829	-1.453923	-2.522576
6	3.727008	-2.334652	-2.666356
1	4.613072	-1.849114	-2.236404
1	3.926297	-2.519887	-3.731866
1	3.573953	-3.303082	-2.167388
6	2.747592	-0.068051	-3.117838
1	1.856842	0.569628	-3.041572
1	3.034916	-0.160630	-4.175922
1	3.561827	0.433881	-2.574319
6	1.307754	-2.127738	-3.238219
1	1.097884	-3.110750	-2.791626
1	1.543243	-2.265546	-4.302690
1	0.397927	-1.512612	-3.171110
6	-2.679760	-0.895918	0.633079
6	-2.641175	-2.297176	0.839455
6	-2.372438	-3.261900	-0.305593
1	-1.748288	-2.735222	-1.041227
6	-1.626762	-4.526172	0.123838
1	-0.730542	-4.287401	0.713775
1	-1.312867	-5.095933	-0.763229
1	-2.267597	-5.189763	0.724047
6	-3.685810	-3.641522	-0.999476
1	-4.355203	-4.158705	-0.294439
1	-3.495995	-4.314344	-1.850013

1	-4.218384	-2.757695	-1.373336
6	-2.917208	-2.794908	2.115825
1	-2.883964	-3.871045	2.290939
6	-3.239610	-1.943309	3.168417
1	-3.451648	-2.351586	4.157912
6	-3.296515	-0.572861	2.950074
1	-3.563745	0.092352	3.774115
6	-3.017465	-0.023649	1.693567
6	-3.156002	1.481289	1.507189
1	-2.786010	1.730736	0.505965
6	-4.632459	1.890326	1.585657
1	-5.246929	1.335134	0.862694
1	-4.745822	2.966287	1.382617
1	-5.039937	1.692246	2.589478
6	-2.325123	2.292618	2.505001
1	-2.594633	2.058660	3.546255
1	-2.503274	3.367239	2.350792
1	-1.249854	2.113245	2.375626
6	-3.156078	-0.753422	-3.482711
1	-2.200857	-0.402314	-3.901072
1	-3.940716	-0.555600	-4.229523
1	-3.088754	-1.842524	-3.338136
6	-5.271897	-0.396585	-1.256080
1	-5.239741	-0.829413	-0.244732
1	-5.718547	-1.141870	-1.930517
1	-5.941828	0.475496	-1.232590
6	-3.506538	1.972066	-2.137233
1	-3.925720	2.512621	-1.275112
1	-4.100091	2.240359	-3.025107
1	-2.478412	2.329653	-2.297263
6	0.104453	3.882317	-0.545346
9	-0.312774	3.667006	-1.781565
9	1.014124	4.836692	-0.551925
9	-0.917816	4.252827	0.201615
7	1.718879	-0.792190	0.845678
7	2.092685	-1.340124	-1.116103
7	-2.334591	-0.362561	-0.655106
8	-0.413830	1.453261	0.087723
8	1.823101	1.906729	-0.865816
8	1.256121	2.633002	1.477760
16	0.853387	2.336842	0.124952
14	-0.646866	-0.031268	-0.896748
1	-0.549004	0.517688	-2.280662

Table S4.8 Geometrical coordinates of DMAP.

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	1.952310	1.129212	0.000012

1	2.527559	2.061201	0.000033
6	0.564165	1.197487	-0.000030
1	0.081816	2.172848	-0.000038
6	-0.185141	-0.000000	-0.000064
6	0.564165	-1.197487	-0.000020
1	0.081816	-2.172848	-0.000016
6	1.952310	-1.129212	0.000019
1	2.527559	-2.061201	0.000046
6	-2.268482	1.254660	0.000057
1	-2.032337	1.860049	0.891621
1	-3.345906	1.056792	-0.000027
1	-2.032256	1.860304	-0.891306
6	-2.268482	-1.254660	0.000042
1	-2.032236	-1.860310	-0.891311
1	-3.345906	-1.056791	-0.000073
1	-2.032358	-1.860042	0.891616
7	2.658389	0.000000	0.000033
7	-1.553078	0.000000	-0.000126

Table S4.9 Geometrical coordinates of **TS3**.

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
5	-0.399732	0.504134	-0.806283
1	-0.094874	1.015728	-1.833164
6	-2.101164	-1.067707	2.629744
6	-2.724651	-2.437747	2.357202
1	-3.332288	-2.411806	1.444456
1	-3.372992	-2.719151	3.200075
1	-1.957394	-3.214953	2.249521
6	-3.229320	-0.049954	2.845368
1	-2.827068	0.946521	3.078867
1	-3.848211	-0.378153	3.691140
1	-3.888369	0.035426	1.970100
6	-1.306559	-1.112533	3.942220
1	-0.663009	-1.992533	4.034270
1	-2.035224	-1.149669	4.764045
1	-0.696550	-0.207515	4.077216
6	-0.064926	-0.882136	1.100087
6	0.721074	-1.809253	1.966625
6	1.586096	-1.332443	2.951756
1	1.693954	-0.259133	3.109906
6	2.296156	-2.230489	3.743802
1	2.981588	-1.856678	4.504875
6	2.136948	-3.603292	3.558610
1	2.702991	-4.304883	4.172822
6	1.262142	-4.079957	2.582648
1	1.145080	-5.152974	2.428067
6	0.552998	-3.183988	1.787035

1	-0.103733	-3.553246	0.996672
6	1.975552	-0.539115	-0.449617
6	2.439117	-2.001871	-0.386586
1	3.325207	-2.104282	-1.025540
1	1.657654	-2.676010	-0.772008
1	2.742901	-2.319239	0.616044
6	2.853616	0.373011	0.403867
1	2.922807	0.042284	1.444912
1	2.485269	1.408432	0.370215
1	3.869869	0.357637	-0.008130
6	2.130257	-0.084767	-1.904766
1	3.161669	-0.305144	-2.208418
1	1.976054	0.995454	-2.020163
1	1.447351	-0.625318	-2.577814
6	0.350447	2.534127	1.705768
1	-0.257696	1.855967	2.315520
6	1.337394	3.290844	2.311604
1	1.484659	3.205818	3.386027
6	2.154039	4.132965	1.514139
6	1.851799	4.161087	0.130384
1	2.424267	4.769802	-0.565329
6	0.832594	3.363748	-0.359351
1	0.621622	3.357348	-1.432615
6	3.473527	4.748870	3.452815
1	2.618406	5.064509	4.071877
1	4.320874	5.399922	3.689975
1	3.744208	3.717344	3.733312
6	4.031475	5.631017	1.166602
1	4.526715	4.991894	0.417983
1	4.806499	6.118747	1.766433
1	3.466417	6.414770	0.637413
6	-4.720469	0.431102	-0.874513
6	-4.712048	1.553550	-1.742665
6	-3.505755	1.923947	-2.601482
1	-2.832051	1.053756	-2.627017
6	-3.903563	2.227524	-4.051410
1	-4.544614	1.440430	-4.473075
1	-3.004277	2.315472	-4.677992
1	-4.449385	3.179529	-4.127941
6	-2.720918	3.114688	-2.031380
1	-3.373548	3.998846	-1.963686
1	-1.878501	3.363602	-2.694485
1	-2.311141	2.928548	-1.028366
6	-5.860710	2.344233	-1.834887
1	-5.856822	3.216658	-2.490722
6	-7.012128	2.036594	-1.119489
1	-7.898903	2.666090	-1.205290
6	-7.028305	0.908687	-0.309948
1	-7.940271	0.649962	0.232169

6	-5.900366	0.092779	-0.173449
6	-6.018195	-1.158021	0.680355
1	-5.005577	-1.561774	0.804769
6	-6.869362	-2.220176	-0.026800
1	-7.899780	-1.856820	-0.160552
1	-6.909971	-3.146363	0.567021
1	-6.473704	-2.467124	-1.021931
6	-6.595804	-0.875321	2.071791
1	-6.078767	-0.043754	2.569511
1	-6.512750	-1.769425	2.708198
1	-7.663581	-0.615873	2.014492
6	-4.575628	-1.558377	-3.226933
1	-5.607971	-1.486210	-2.857124
1	-4.511341	-2.410339	-3.920495
1	-4.363494	-0.639737	-3.793293
6	-3.555106	-3.433548	-0.993690
1	-2.717609	-3.652621	-0.315515
1	-3.559180	-4.215351	-1.769768
1	-4.491895	-3.518772	-0.425301
6	-1.584793	-1.773568	-2.541695
1	-1.323601	-0.838440	-3.058841
1	-1.507667	-2.590896	-3.276142
1	-0.817395	-1.968096	-1.774928
7	-1.332703	-0.606397	1.415019
7	0.492035	-0.365229	-0.033070
7	0.087107	2.551035	0.396542
7	-3.522141	-0.367396	-0.743014
7	3.171090	4.857535	2.041175
14	-2.181304	0.427780	0.042323
1	-2.701519	1.618526	0.735656
14	-3.330324	-1.767386	-1.842822
6	7.548197	-1.212292	-1.799494
9	7.877922	-2.498594	-1.731917
9	7.850035	-0.775168	-3.019400
9	8.305864	-0.548302	-0.929498
8	5.583803	0.489514	-1.585889
8	5.089878	-1.775062	-2.456611
8	5.621571	-1.454965	-0.057082
16	5.759501	-0.961274	-1.432356

Table S4.10 Geometrical coordinates of TS4.

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
5	0.305675	0.056268	-0.995055
1	0.407579	0.760762	-1.939572
6	-1.405179	-2.174243	2.010695
6	-2.819021	-2.745015	1.894036
1	-3.519458	-1.975354	1.544954

1	-3.150016	-3.089705	2.884724
1	-2.862722	-3.601835	1.209484
6	-1.437379	-1.048351	3.051648
1	-0.448715	-0.578625	3.157523
1	-1.735612	-1.470072	4.020801
1	-2.169794	-0.275888	2.787031
6	-0.452423	-3.245380	2.563571
1	-0.593839	-4.229109	2.104790
1	-0.658590	-3.352919	3.637208
1	0.597807	-2.936898	2.454458
6	-0.237822	-2.164317	-0.251192
6	-0.219912	-3.660335	-0.295710
6	0.900984	-4.423488	0.039686
1	1.808282	-3.939323	0.399371
6	0.851651	-5.811647	-0.050414
1	1.728452	-6.401642	0.218663
6	-0.315271	-6.446032	-0.478985
1	-0.348904	-7.533710	-0.554369
6	-1.438526	-5.688026	-0.806822
1	-2.352197	-6.178411	-1.144910
6	-1.391306	-4.299380	-0.709308
1	-2.257476	-3.697795	-0.992245
6	1.086533	-2.007890	-2.444343
6	0.349856	-3.207458	-3.071815
1	0.731946	-3.318531	-4.095113
1	-0.733557	-3.033017	-3.146037
1	0.524825	-4.160427	-2.562228
6	2.529729	-2.398306	-2.109155
1	2.573056	-3.231869	-1.397383
1	3.075087	-1.531106	-1.717594
1	3.020895	-2.735278	-3.034061
6	1.132662	-0.926519	-3.535592
1	1.597920	-1.378748	-4.421611
1	1.733006	-0.060223	-3.243158
1	0.121221	-0.598325	-3.815043
6	-3.226008	1.971090	0.282174
6	-2.782894	3.125623	-0.409905
6	-1.795532	3.057389	-1.566537
1	-1.731100	2.010518	-1.896304
6	-2.227990	3.891873	-2.775921
1	-3.238604	3.631231	-3.122619
1	-1.524769	3.730878	-3.605632
1	-2.218084	4.967939	-2.547933
6	-0.395486	3.484138	-1.113240
1	-0.391056	4.545624	-0.819527
1	0.352069	3.343925	-1.907081
1	-0.042662	2.908923	-0.245354
6	-3.245507	4.378144	0.004579
1	-2.899734	5.271774	-0.518635

6	-4.138916	4.509028	1.061461
1	-4.492436	5.495865	1.364069
6	-4.576809	3.371604	1.728868
1	-5.281641	3.470266	2.557818
6	-4.129488	2.099212	1.360086
6	-4.647768	0.893055	2.122737
1	-4.083865	0.022389	1.760653
6	-6.132355	0.645057	1.834649
1	-6.743741	1.485650	2.197992
1	-6.480519	-0.270220	2.338590
1	-6.322141	0.539033	0.756878
6	-4.411563	1.023740	3.631013
1	-3.367333	1.285042	3.855363
1	-4.652048	0.079149	4.143396
1	-5.049709	1.807874	4.065775
6	-5.001064	1.140394	-2.033511
1	-5.671858	1.491672	-1.235555
1	-5.611658	0.687744	-2.829815
1	-4.493532	2.023870	-2.445062
6	-4.704267	-1.628039	-0.812341
1	-4.049231	-2.481868	-0.591979
1	-5.396523	-1.935333	-1.612154
1	-5.300645	-1.418924	0.088101
6	-2.628618	-0.659000	-2.806503
1	-2.236164	0.208586	-3.358879
1	-3.174363	-1.301764	-3.514673
1	-1.764577	-1.228313	-2.434116
7	-0.955762	-1.554818	0.702508
7	0.391794	-1.433800	-1.200783
7	-2.778153	0.663472	-0.137616
14	-1.122605	0.274462	0.338838
1	-0.927592	1.090001	1.548925
14	-3.753520	-0.109808	-1.403938
8	2.615396	0.468477	-1.200571
16	3.037981	1.853911	-1.523645
8	2.884637	2.206058	-2.931356
8	2.621580	2.859440	-0.545103
6	4.860266	1.738182	-1.257399
9	5.457331	2.888807	-1.538017
9	5.390534	0.793832	-2.028192
9	5.133851	1.429546	0.011348
6	2.344517	-0.965174	1.280759
1	2.122587	-1.901338	0.758951
6	3.490069	-0.874815	2.048524
1	4.135072	-1.745138	2.144380
6	3.831450	0.372611	2.626154
6	2.930251	1.433096	2.395932
1	3.121406	2.439067	2.760551
6	1.809674	1.217458	1.612751

1	1.160117	2.059440	1.366856
6	5.909064	-0.555363	3.470572
1	5.444710	-1.409553	3.989679
1	6.770958	-0.229235	4.062544
1	6.276984	-0.906936	2.491278
6	5.345564	1.869932	3.786351
1	5.421771	2.578454	2.944848
1	6.318481	1.824829	4.287238
1	4.609640	2.266187	4.504518
7	1.499044	0.040527	1.069415
7	4.982640	0.545066	3.330892

Table S4.11 Geometrical coordinates of **4.16**.

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
5	-0.031674	0.329725	-0.466128
1	0.004035	0.836058	-1.558940
6	-2.485409	-2.034056	1.967007
6	-3.638409	-2.835810	1.358303
1	-4.241531	-2.195612	0.701915
1	-4.286794	-3.208319	2.165212
1	-3.285997	-3.702576	0.786302
6	-3.099217	-0.910827	2.813429
1	-2.324426	-0.347424	3.352666
1	-3.781244	-1.356387	3.550107
1	-3.683103	-0.208356	2.203726
6	-1.684142	-2.913836	2.940615
1	-1.522029	-3.930048	2.568346
1	-2.250740	-2.996085	3.878760
1	-0.711235	-2.457427	3.178318
6	-0.610732	-1.967095	0.228638
6	-0.523950	-3.464300	0.221590
6	0.371498	-4.182357	1.016100
1	1.007793	-3.661889	1.731322
6	0.440029	-5.569376	0.910881
1	1.144338	-6.124028	1.531878
6	-0.385202	-6.245958	0.012705
1	-0.322753	-7.331518	-0.074481
6	-1.291723	-5.533378	-0.771403
1	-1.939055	-6.056632	-1.476022
6	-1.362174	-4.146736	-0.663582
1	-2.053230	-3.580217	-1.292373
6	1.446237	-1.764225	-1.255590
6	1.157685	-3.023702	-2.091332
1	1.965751	-3.114265	-2.828988
1	0.210189	-2.931561	-2.643297
1	1.147025	-3.952483	-1.511685
6	2.590987	-2.017441	-0.271831

1	2.339191	-2.793384	0.459559
1	2.889620	-1.099302	0.253241
1	3.482412	-2.332732	-0.830182
6	1.921526	-0.701535	-2.255305
1	2.819003	-1.092595	-2.749801
1	2.246298	0.224782	-1.769142
1	1.150218	-0.477821	-3.005841
6	1.361496	0.546834	1.659596
1	0.692686	-0.226144	2.046747
6	2.441715	0.971901	2.387006
1	2.627108	0.515241	3.355144
6	3.331641	1.938213	1.834087
6	2.939650	2.501415	0.590186
1	3.559772	3.224964	0.071206
6	1.860691	1.988522	-0.076003
1	1.611596	2.324764	-1.082144
6	4.982046	1.439208	3.507734
1	4.297866	1.445552	4.368837
1	5.946096	1.832517	3.845607
1	5.122777	0.408303	3.143156
6	5.420400	3.126997	1.712089
1	5.626676	2.713065	0.714242
1	6.355630	3.180493	2.277933
1	5.017833	4.146125	1.608973
6	-4.082411	1.834337	-0.061371
6	-3.576010	3.119605	-0.378456
6	-2.281784	3.323732	-1.155187
1	-1.984635	2.354273	-1.581992
6	-2.453248	4.304064	-2.321607
1	-3.312336	4.040103	-2.954252
1	-1.549343	4.307197	-2.948268
1	-2.605818	5.333037	-1.963345
6	-1.147639	3.804146	-0.240950
1	-1.417076	4.761933	0.230880
1	-0.225031	3.959761	-0.819432
1	-0.929510	3.089246	0.565619
6	-4.290426	4.251357	0.025133
1	-3.892954	5.242082	-0.204665
6	-5.499781	4.142946	0.700778
1	-6.045207	5.038026	1.003288
6	-6.012852	2.881436	0.972368
1	-6.974011	2.790280	1.483141
6	-5.325972	1.720114	0.603412
6	-5.978646	0.378411	0.888188
1	-5.226456	-0.395280	0.683955
6	-7.169916	0.143961	-0.048754
1	-7.953376	0.896123	0.131659
1	-7.610560	-0.851431	0.118639
1	-6.878403	0.216665	-1.106001

6	-6.427599	0.236422	2.346732
1	-5.629172	0.513167	3.048842
1	-6.728632	-0.801981	2.554346
1	-7.296103	0.877272	2.560953
6	-4.732919	1.153469	-2.995624
1	-5.622938	1.507656	-2.456046
1	-5.055871	0.704286	-3.947109
1	-4.115437	2.034199	-3.226353
6	-4.678210	-1.713132	-1.870123
1	-4.034609	-2.515283	-1.481135
1	-4.998874	-2.008292	-2.881942
1	-5.574031	-1.660686	-1.236388
6	-2.161111	-0.496324	-2.961290
1	-1.589819	0.407859	-3.215906
1	-2.449449	-0.996757	-3.899425
1	-1.483323	-1.173563	-2.418634
7	-1.633974	-1.375138	0.910766
7	0.227199	-1.233454	-0.493041
7	1.080152	1.003229	0.420627
7	-3.337235	0.658296	-0.437727
7	4.481625	2.276921	2.432787
14	-1.821293	0.391229	0.421923
1	-1.917664	1.223329	1.647297
14	-3.730620	-0.087322	-2.007796
6	7.218179	0.377438	-0.758589
9	7.746101	-0.753309	-0.305638
9	7.699884	0.607271	-1.972081
9	7.628860	1.366968	0.040987
8	4.987966	1.606936	-1.294189
8	5.103369	-0.844772	-1.664912
8	5.061204	0.071003	0.647187
16	5.374998	0.286191	-0.778165

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