Synthesis, Reactivity, and Catalytic Applications of Compounds with Heavier Group 14 Elements in Usual and Low Oxidation State

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CHEMICAL SCIENCES

by

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CERTIFICATE

This is to certify that the work incorporated in this Ph.D. thesis entitled **"Synthesis, Reactivity, and Catalytic Applications of Compounds with Heavier Group 14 Elements in Usual and Low Oxidation State"** submitted by **Mr. V. S. V. S. N. Swamy** (AcSIR Registration Number 10CC14A26023) to Academy of Scientific and Innovative Research (AcSIR) in fulfillment of the requirements for the award of the Degree of the Doctor of Philosophy, embodies original research work under my supervision at Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory (CSIR-NCL), Pune, India. I further certify that this work has not been submitted to any other University or Institution in part or full for the award of any degree or diploma. Research material obtained from other sources has been duly acknowledged in the thesis. Any text, illustration, table etc., used in the thesis from other sources, have been duly cited and acknowledged.

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DECLARATION

I hereby declare that the original research work embodied in this thesis entitled **"Synthesis, Reactivity, and Catalytic Applications of Compounds with Heavier Group 14 Elements in Usual and Low Oxidation State"** submitted to the Academy of Scientific and Innovative Research (AcSIR), New Delhi, for the award of degree of **Doctor of Philosophy** in **Chemical Sciences** is the outcome of experimental investigations carried out by me under the supervision of **Dr. Sakya Singha Sen**, Senior Scientist, CSIR-National Chemical Laboratory (CSIR-NCL), Pune. I affirm that the work incorporated is original and has not been submitted to any other academy, university or institution in part or full for the award of any degree or diploma.

Date: 1st March, 2019
Place: CSIR-NCL, Pune

V. S. V. S. N. Swamy
(Research Scholar)

This dissertation is dedicated to
my beloved parents

Amma Nannalaku Prematho…….....

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V. S. V. S. N. Swamy

Abbreviations

Units and standard terms

Anal.	Analysis
BDE	Bond Dissociation Energy
Calcd.	Calculated
CCDC	Cambridge Crystallographic Data Centre
CIF	Crystallographic Information file
°C	Degree Centigrade
DFT	Density Functional Theory
Mg	Milligram
H	Hour
Hz	Hertz
mL	Millilitre
min	Minute
mmol	Millimole
M.P.	Melting Point
NPA	Natural Population Analysis
Ppm	Parts per million
%	Percentage

Chemical Notations

Ad	Adamantyl

Ar	Aryl
C_6D_6	Dueterated benzene
$CDCl_3$	Deuterated chloroform
DCM	Dichloromethane
Dipp	Diisopropylaniline
DMSO	Dimethyl sulfoxide
EtOH	Ethanol
EtOAc	Ethyl Acetate
HBpin	Pinacolborane
*i*Pr	Isopropyl
MeOH	Methanol
Me	Methyl
Mes	2, 4, 6 –trimethylbenzene
n-BuLi	*n*-butyllithium
NHC	*N*-Heterocyclic Carbene
NHSi	*N*-Heterocyclic Silylene
NHGe	*N*-Heterocyclic Germylene
Np	Neopentyl
PhLi	Phenyllithium
*t*Bu	Tertiary butyl
py	Pyridine
THF	Tetrahydrofuran
TMSCl	Trimethylsilylchloride

TMSCN	Trimethylsilyl cyanide

Other Notations

δ	Chemical shift
J	Coupling constant in NMR
Equiv.	Equivalents
HRMS	High Resolution Mass Spectrometry
NMR	Nuclear Magnetic Resonance
rt	Room temperature
UV	Ultraviolet
VT	Variable temperature
XRD	X-Ray Diffraction

General Remarks

- Independent compound and reference numbering have been used for each chapter.
- All chemicals were purchased from commercial sources and used as received.
- All reactions were carried out under inert atmosphere following standard procedures using Schlenk techniques and glovebox.
- Deuterated solvents for NMR spectroscopic analyses were used as received. All ^{1}H NMR and ^{13}C NMR analysis were obtained using a Bruker or JEOL 200 MHz, 400 MHz or 500 MHz spectrometers. Coupling constants were measured in Hertz. All chemical shifts are quoted in ppm, relative to TMS, using the residual solvent peak as a reference standard.
- IR spectra were recorded on Shimadzu FT-IR-8300 spectrometer as thin films in chloroform using NaCl plates and absorptions were expressed in cm^{-1}.
- HRMS spectra were recorded at UHPLC-MS (Q-exactive-Orbitrap Mass Spectrometer) using electron spray ionization [(ESI^{+}, +/− 5kV), solvent medium: acetonitrile and methanol] technique and mass values are expressed as *m/z*. GC-HRMS (EI) was recorded in Agilent 7200 Accurate-mass-Q-TOF.
- All the reported melting points are uncorrected and were recorded using Stuart SMP-30 melting point apparatus.
- The solvent used were purified by an MBRAUN solvent purification system MBSPS-800.
- Column chromatography was performed on silica gel (100-200 mesh size).
- Chemical nomenclature (IUPAC) and structures were generated using ChemDraw Professional 15.1.

Synopsis of the Thesis to be submitted to the Academy of Scientific and Innovative Research for Award of the Degree of Doctor of Philosophy in Chemistry	
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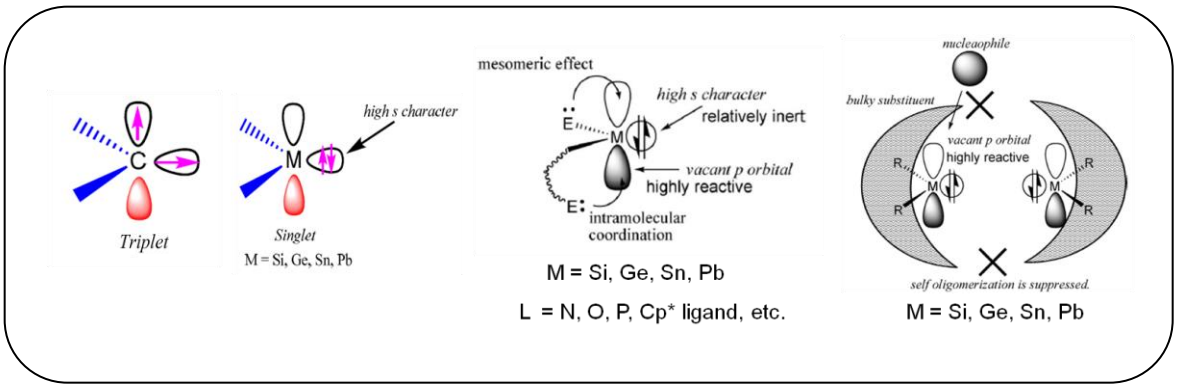
Keywords: *Low-Valent Group 14 compounds, Ge(II) dication, silylene, C–F bond activation, Catalysis.*

This thesis mainly focuses on the synthesis, reactivity, and catalytic application of compounds with heavier group 14 elements in usual and low oxidation state. The current thesis comprises of five chapters, out of which the first is the introductory chapter. The first chapter describes the general introduction; stabilization and significance of heavier group 14 metallylenes with the recent literature precedents. The second chapter to fifth chapters is working chapters which narrate the specific synthesis, reactivity, and catalytic application of compounds with heavier group 14 elements in usual and low oxidation state. The second chapter describes the stabilization of a Ge(II) dication using isocyanide as ligands. In the third chapter, the Si(II) compound (LSiN-$(SiMe_3)_2$, L = PhC(N*t*Bu)$_2$) was showed to activate the inert bond activations such as the C(sp^3)–H and C(sp^3)–F bond of acetophenone and 1,1,1-trifluoroacetophenone. We also discussed the scope of C(sp^2)–F bond activation of C_6F_6 and $C_6F_5CF_3$ at the Si(II) center. Synthesis and characterization of a neutral penta-coordinate Si(IV) compound and its potential use in aldehyde cyanosilylation at ambient condition, and this was explained in chapter four. The final chapter explores the B–H and C=O bond activation and subsequent application of Si(II) compound (LSiN-$(SiMe_3)_2$, L = PhC(N*t*Bu)$_2$) as a single-site catalyst. Herein, a Si(II) compound, discussed in fifth chapter has been utilized for hydroboration and cyanosilylation of carbonyl compounds and aldehydes, respectively.

Chapter-1: General Introduction: Stabilization and Significance of Heavier Group 14 Metallylenes

The fundamental understanding of the reactivity of main-group (MG) compounds have been challenged and importantly developed over recent decades. Generally, main-group element higher than of the third row displays abnormal physical and chemical properties. Considering the rich chemistry displayed by compounds with heavier group 14 elements in usual and low oxidation state, it has become one of the most important areas of modern inorganic chemistry with continuous developments. In this chapter, we mainly focused on the scope of heavier group 14 metallylenes (R_2M, M = Si, Ge, Sn, Pb) and their significant applications in small molecule activation (especially H_2 and NH_3) as well as in homogeneous catalysis with the recent literature precedents. In contrast to methylene (CH_2), heavier methylene analogues (SiH_2, GeH_2, SnH_2 and PbH_2) have singlet ground state rather than triplet state (See in Scheme 1). After the crystalline *N*-heterocyclic carbene made by Arduengo and his coworkers, the heavier group 14 metallylenes explored by taking the advantages of electronic and steric stabilization. In the case of electronic stabilization the covalently bound ligands associated with donor atoms partly donate their electronic density into a highly reactive vacant coordination site, and thereby minimizing the electrophilicity of a vacant orbital. In another case, the sterically bulky ligands attached to a central atom to shield the vacant coordination site from the outer nucleophilic attack or solvent molecules, and therefore, suppress the propensity of the polymerization and oligomerization of their corresponding monomer units.

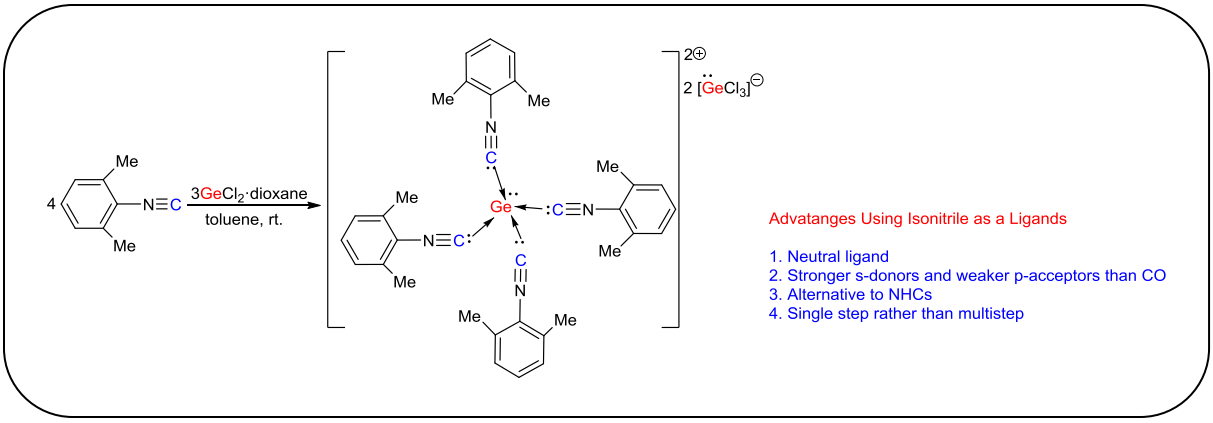


Scheme 1. General outlook of electronic and steric stabilization of metallylenes.

The recent developments demonstrate that the low-valent heavier group 14 compounds can mimic the chemistry of the transition metal. For example, Aldridge's two coordinate acyclic silylenes were demonstrated for both dihydrogen and ammonia activation at room temperature. This is because of the lower singlet-triplet gaps, which is almost akin to those of transition metal based systems. Moreover, a handful number of reports have recently been published, where a compound with the heavier group elements used as a single component catalyst. The thesis describes unique synthetic methodologies for the easy access of low-valent heavier group 14 compounds, their reactivity and catalytic application in some important organic transformations. The overall work embodied in this thesis has been divided into four working chapters described as below.

Chapter-2: **Synthesis of a Ge(II) Dication by Using Isocyanide Ligands**

Recent studies demonstrated that the utilization of the cations and dications of heavier group 14 elements in various catalytic transformations and small molecule activation seems to be attractive and promising. This is beacuse of the central atom in these compounds having two or three unoccupied valence orbitals as well as holds a lone pair of electrons. Consequently, the central atom possesses an ambiphilic character, which is usually helpful for small molecule activation. In order to search for neutral ligands for isolating the low-valent main group compound/cation, we have for the first time introduced isocyanides as a potentional neutral ligands for stabilizing the Ge(II) dication, in a single step. In this chapter, we present the reaction of 2, 6-dimethylphenylisocyanide with $GeCl_2$ leads to the formation of a Ge(II) dication (Scheme 2) with two [$GeCl_3$] molecules as counter anions.

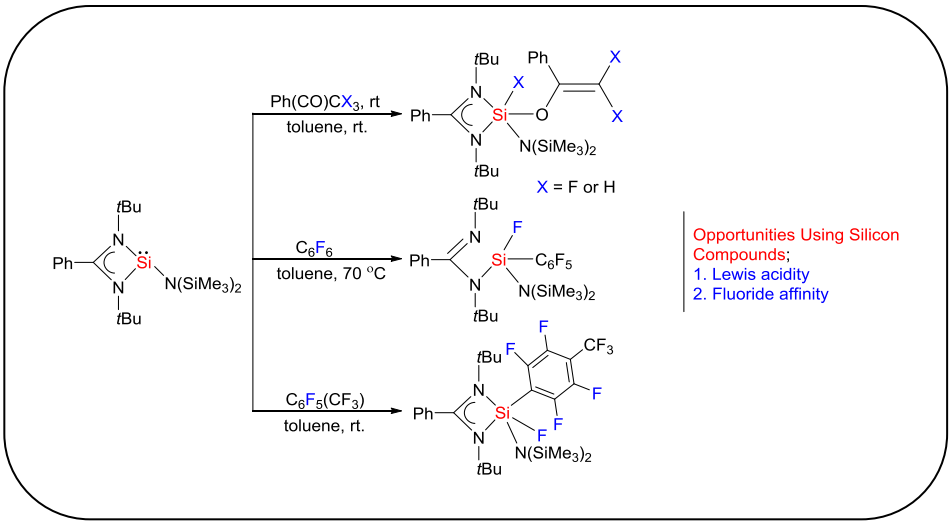


Scheme 2. Synthesis of Ge(II) dication.

The composition of the final crystalline compound was supported by single crystal X-Ray studies and multi-nuclear NMR spectroscopy. The dicationic Ge(II) center is tetrahedrally bound to four isocyanide ligands and also holds a stereochemically inactive lone pair of electron. DFT calculations revealed that the dication is stabilized only by σ-donation from the four isocyanide ligands. Furthermore, Natural population analysis gives a charge of +0.74 on the Ge(II) center, indicating that the positive charge is shared by the isocyanide ligands.

Chapter-3: **Preparation of Silicon (II) bis(trimethylsilyl)amide: Towards C(sp^3)–F, C(sp^2)–F and C(sp^3)–H Bond Activation**

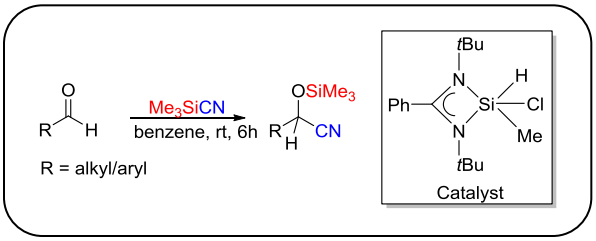
The formation and cleavage of C–F bonds is of great interest in medicinal and environmental chemistry. For example, on an average about 20% of pharmaceuticals and 40% of agrochemicals have C-F bonds. This is presumably because the chemical inertness and high thermal stability of fluorocarbons, which makes the C–F bond (544 KJ/mol) one of the strongest bond in organic chemistry. Consequently, the molecules with C–F bond are extremely long-lived and potentially toxic. The inherent Lewis acidic nature as well as affinity towards fluorine prompted us to use a silylene for aliphatic C–F bond activation. Herein, we utilized a silicon (II) bis(trimethylsilyl)amide (LSiN-$(SiMe_3)_2$, L = PhC(N*t*Bu)$_2$) compound for C-F bond activation (Scheme 3). DFT studies revealed that the reaction is initiated *via* a nucleophilic attack from the oxygen to the silicon atom followed by C–F/H bond cleavage. We also showed that silylene can react with one of the C(sp^2)–F bonds of C_6F_6 and the para C–F bond with respect to the CF_3 substituent in $C_6F_5CF_3$.



Scheme 3. $C(sp^3)$–F, $C(sp^2)$–F and $C(sp^3)$–H bond activations by silylene.

Chapter-4: **Selective Aldehyde Cyanosilylation by a Neutral Penta-Coordinate Silicon Compound**

Compounds of composition R_3SiX (R = organic substituent, X = electronegative group) have long been utilized as catalysts for several organic reactions, mainly in carbon–carbon bond-forming processes such as Diels–Alder reaction, aldol condensation. This is due to the tendency of the silicon atom to expand its valence shell, giving rise to five- and six-coordinate intermediates, which is of a great interest for catalysis. In this chapter, we present the synthesis of a Si(IV) hydride ($PhC(NtBu)_2SiH(CH_3)Cl$) using an amidinato ligand and explored its potential as a catalyst (optimum conditions; 3 mol%, 6 h, benzene, room temperature) for the cyanosilylation of a variety of aldehydes at room temperature giving good yield (Scheme 4). The Si(IV) catalyst showed broad substrate scope, as well as functional group tolerance (ester, amide, halides, and acid) with an excellent selectivity of this process, make it attractive for facile synthesis of cyanosilylated products which are of high utility in various research areas. Moreover, we also demonstrated the mechanism of aldehyde cyanosilylation by spectroscopic studies. As the elimination of halosilane initiate the catalytic cycle, this approach will prompt to use halogenated silicon compounds as Lewis acid catalysts for other organic transformations.

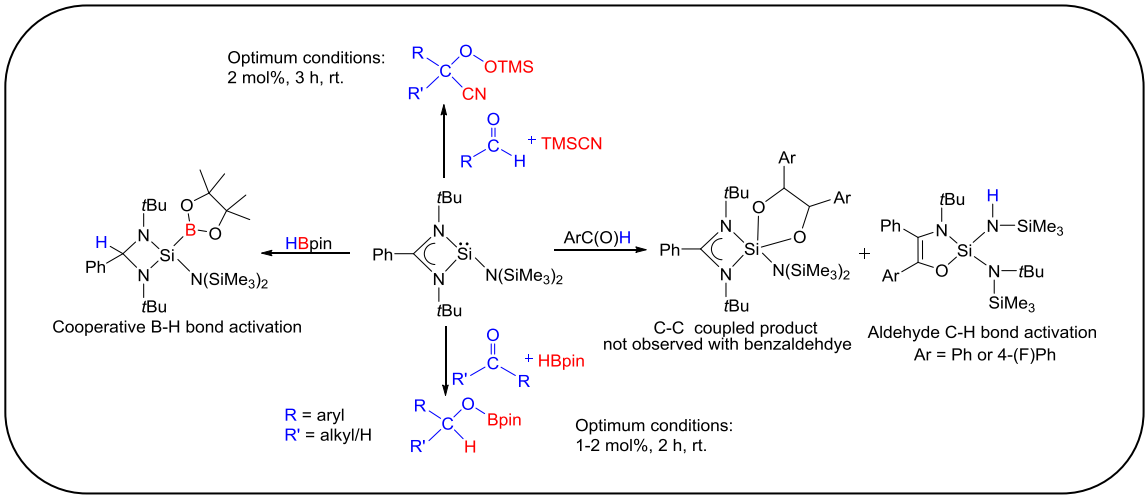


Scheme 4. Silicon(IV) hydride mediated cyanosilylation of aldehydes.

Chapter-5: **B–H and C=O Bond Activation by Silylene and Subsequent Use as a Single-site Catalyst**

The use of silylene is limited to small molecule activation. Extending silylene from a stoichiometric reagent to a catalyst is the "Holy Grail" in contemporary main group chemistry. We have reported in this chapter the use of a well-defined silylene as a single component catalyst for hydroboration reaction as well as cyanosilylation, under mild reaction condition. Silylene, $PhC(NtBu)_2SiN(SiMe_3)_2$, was chosen as a catalyst due to its easy synthetic accessibility and

stability. We have started our study by stoichiometric reactions of silylene with both aldehydes and pinacolborane (HBpin) at ambient conditions (See in Scheme 5). We also discussed the mechanism of hydroboration by silylene with the help of DFT studies. Moreover, we extended the catalytic efficacy of silylene applied for aldehyde cyanosilylation under mild condition. In both the cases, the Si(II) catalyst showed broad substrate scope, as well as good functional group tolerance (ester, amide, halides, and acid) with a good selectivity of this process, make it attractive for facile synthesis of organoborate esters and cyanosilylated products of high utility in organic synthesis.



Scheme 5. B–H and C–H bond activation by silylene and subsequent use as single-site catalyst for hydroboration and cyanosilylation.

Table of Contents

General Introduction

Abstract

This chapter provides an overview about the fundamental interest and formidable synthetic challenge regarding the synthesis of compounds with heavier low-valent group 14 elements and a general introduction covering a brief description of important compounds in this research area is provided. The aim and the results presented in this contribution are outlined.

1.1. Classification of Group 14 Compounds

The chemistry of group 14 elements has become one of the most important areas of modern inorganic chemistry and is still an area of continuous investigation. Generally, main-group elements above the second row are classified as "heavy main group elements" and some of them can display abnormal physical and chemical properties.[1] The valence shell electronic configuration of these elements is ns^2np^2 which allows them to connect with four bonds and then it forms the neutral compounds. Basically, the group 14 elements shows two types of oxidation states i.e. +2 and +4 (Figure 1).[2] Compounds with +4 oxidation state are more common for carbon, silicon, and germanium, whereas tin and lead are more stable in the +2 oxidation state due to inert pair effect (in which the element has both non bonding electrons and vacant orbitals).

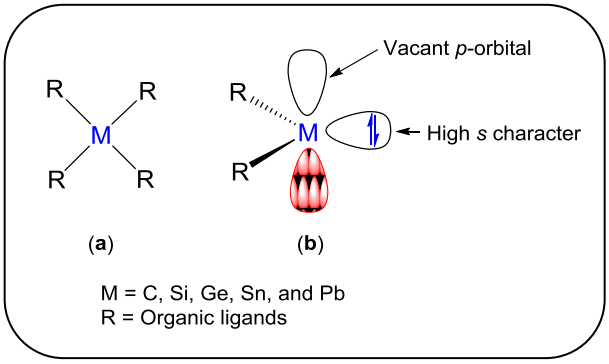


Figure 1. (a) Compounds with (IV) oxidation state and (b) Compounds with (II) oxidation state.

In addition, the group 14 elements have different properties ranging from non-metallic to metallic. Carbon is the lightest element and true non-metal and it can exist in various allotropic forms (generally diamond, graphite and fullerenes). Furthermore, carbon is followed by the two metalloids, silicon and germanium. The remaining elements (tin and lead) are both metallic in nature.[3] The compounds of group 14 elements in +4 oxidation state have many synthetic applications such as catalyst precursors or for the preparation of catalysts. For example, saturated silicon compounds with leaving groups can be utilized in the catalytic application of C-C bond forming reactions.[4] Recently, there has been significant progress in stabilizing main group *p*-block elements in low oxidation states with the hope of mimicking "transition-metal like" chemistry with them.[5] This thesis is mainly focused on the stabilization of low-valent group 14 compounds, small molecule activation, and their application in homogeneous catalysis.

1.2. Stabilization of Heavier Low-valent Main Group 14 Compounds

In contrast to the carbon, the stability of heavier carbene congeners H_2M: (M = Si, Ge, Sn, and Pb) increases while going down the group due to inert pair effect.[6] In case of heavier carbon analogues, dichloroplumbylene ($PbCl_2$) and dichlorostannylene ($SnCl_2$) can be considered as very stable ionic compounds at ambient conditions but they also exist as ion pairs or polymeric form in solution as well as in the solid state. The dichlorogermylene complex $GeCl_2$·dioxane[7] shows moderate stability; whereas the compounds of divalent silicon are hardly isolable without the usage of the advantage of both electronic and steric protection.[8] The heavier carbene congeners are more stable in singlet state, unlike the triplet state of carbene. This is because of the outermost *s* orbital (ns^2) electrons of divalent species, which are tightly bound to the nucleus as compared to carbon atom. Consequently, it is difficult for them to participate in bonding and shows (ns^2) (np^2) valence shell electronic configuration in their divalent compounds.[9]

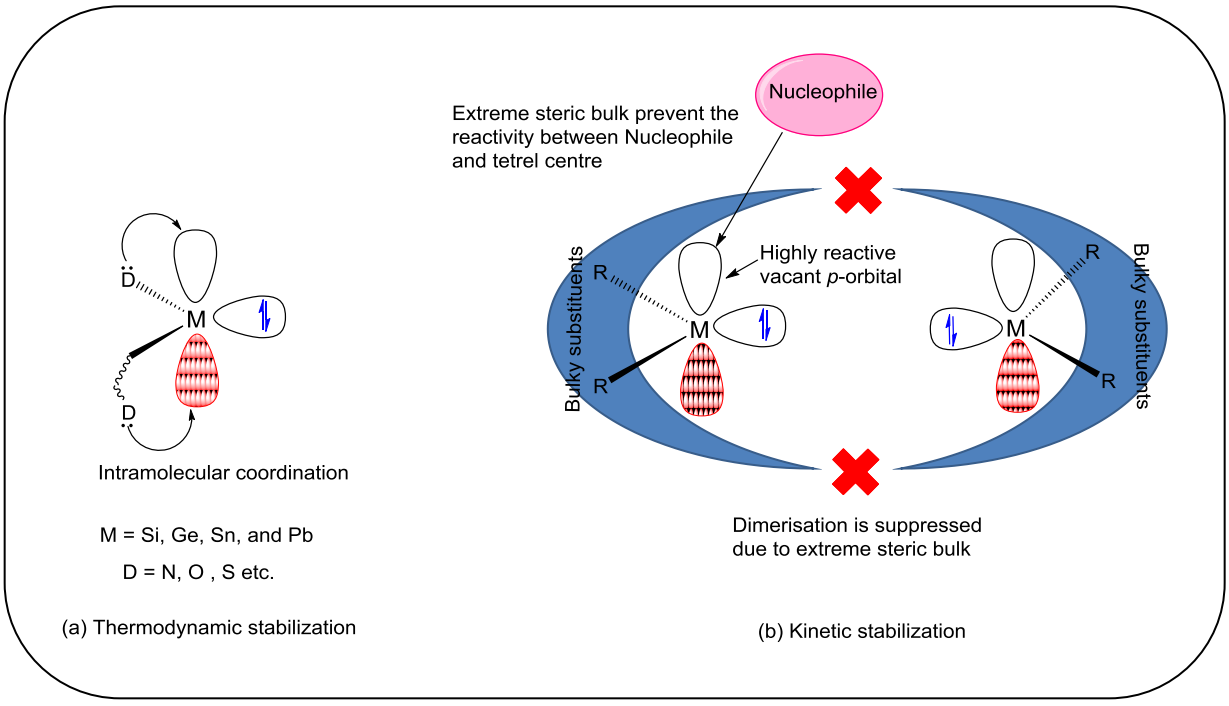


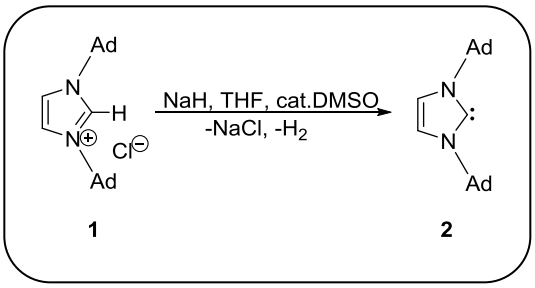
Figure 2. (a) Thermodynamic stabilization using Lewis base; and (b) kinetic stabilization using bulky substituents.

The vacant *p*-orbitals on group 14 elements are responsible for their high reactivity. On this basis, these have the tendency towards dimerization. In order to stabilize them, the highly

reactive vacant *p*-orbital could be protected by the use of both electronic donation and sterically bulky ligands. These strategies are summarized in the Figure 2. In case of the thermodynamic stabilization, the hetero donor atom (such as N, O, S) bound to the central atom donates its electron density to the empty *p*-orbital of central atom.[10] Consequently, it reduces the electrophilicity of vacant *p*-orbital and it shows almost inertness towards nucleophiles during the reactions. The introduction of bulky ligands provides the steric protection of reactive *p*-orbitals from other molecules and inhibits the dimerization.

1.3. Low-valent Chemistry of Silylene and Germylene

Arduengo and coworkers isolated the first stable and structurally authenticated *N*-heterocyclic carbene (NHC) in 1991.[11] The compound **2** was synthesized by reduction of 1,3-di-1-adamantylimidazoliumchloride, **1** with sodium hydride (Scheme 1). The key stabilization of **2** can be attributed to the "push and pull effect" of nitrogen atoms, which allows the transfer of electron density from the nitrogen atoms to the vacant *p*-orbital of the carbon center. Consequently, it reduces the electrophilicity and increases its thermodynamic stability at the carbon center.[12] Additionally, the bulky substituents on the nitrogen atoms make the carbon center more kinetically stable. Subsequent to Arduengo's ground-breaking discovery, several new families of stable *N*-heterocyclic carbenes (NHCs) have been reported. The strategy was further extended for the stabilization of various heavier low-valent group 14 compounds.



Scheme 1. Synthesis of the first stable *N*-heterocyclic carbene.

Carbenes have many useful applications in organometallic chemistry, organic synthesis, and homogeneous catalysis.[13] Therefore, the study of heavier carbene analogs such as silylene,[14] germylene,[15] and stannylene[16] has become one of the most attractive research domains in modern organometallic chemistry.

1.3.1. Silylenes

Silylenes, are divalent heavier carbene congeners and found as transient species in 1964 by Skell and Goldstein.[17] After Arduengo's isolation of a stable NHC carbene, West and coworkers realized the first isolable and thermally stable (up to 150 °C) *N*-heterocyclic silylene (**3a-3d**) by the reduction of the corresponding dichlorosilane with elemental potassium.[14] In continuation of this work, saturated backbone of NHSi **4a-e**,[18] benzo- and pyrido-fused NHSis (**5a-b**[19a,b] and **5c**[19c] respectively) were also synthesized by reducing the respective dichlorido derivatives.

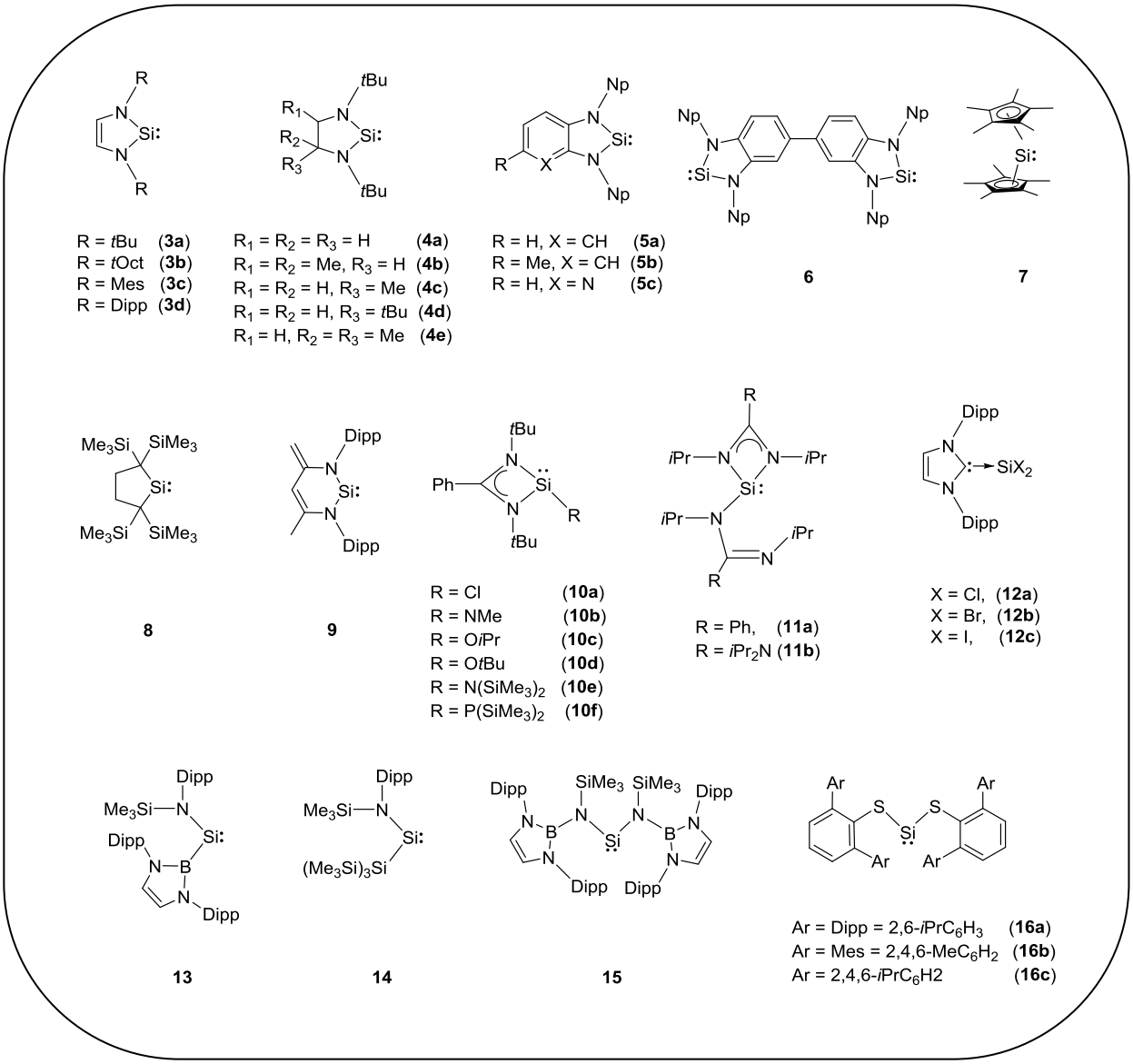


Chart 1. Selected examples of silylenes.

The bis-silylene-based biphenyl moiety **6** was reported by Lappert et al. in 2005.[20] The first decamethylsilicocene **7** was synthesized by Jutzi et al. in 1989 by utilizing the advantage of η^5-coordination of pentamethylcyclopentadienyl ligand.[21a] In 1999, the cyclic dialkylsilylene **8** was reported by Kira and coworkers, where the silicon center was kinetically stabilized by the bulky helmet-like bidentate substituents.[21b] In 2006, Driess et al. synthesized the six-membered NHSi **9** by using a *β*-diketiminate-like backbone. Interestingly, this silylene has two nucleophilic centers, one is at Si(II) and the other is at the CH_2 carbon moiety of backbone.[22] Roesky et al. reported the first three coordinate amidinato based silylene chloride **10a** in 2006. In the following years, a series of functionalized silylenes **10a-f** [23] were structurally characterized by various research groups (Chart 1). In 2012, Tacke et al. synthesized silylenes **11a** and **11b** that were stabilized by *N*,*N*-di(iso-propyl)amidinato and guanidinato ligands, respectively.[24] The nitrogen based ligands have extensively studied than other donor atoms such as carbon, oxygen, phosphorous, and boron based systems. Although the dihaloderivatives of silicon are unstable, the groups of Roesky and Filippou stabilized dihalo silylene moieties (**12a-c**) by using the NHC carbene ligands.[25b-d] More recently, the groups of Aldridge, Jones, and Mountford synthesized the stable mixed amido boryl silylene $Si(B(NArCH)_2)(N(SiMe_3)Dipp)$ **13** and hyper silyl substituted $Si(Si(SiMe_3)_3)(N(SiMe_3)Dipp)$ **14**, respectively.[26] Similarly, Aldridge and Power isolated the acyclic silylenes {(2,6(2,4,6-(N(B(NArCH)$_2$)(SiMe$_3$))Si: **15** and $Me_3C_6H_2)_2$-C_6H_3)S}Si: **16a-c,** which were readily reactive towards NH_3 and gave the respective oxidative products but unable to split the dihydrogen due to their larger HOMO-LUMO energy gap.[25a,27]

1.3.2. Germylenes, germanium dications

As compared to the analogues of carbene and silylene, germylenes are less reactive due to their large *sp* separation gap of germanium center.[28] Lappert et al. in 1976 reported the first stable acyclic germylene $[(Me_3Si)_2N]_2Ge$ at an ambient condition. In a subsequent report, the same group isolated the alkyl-germylene, $[(Me_3Si)_2CH]_2Ge$: by introducing bulky alkyl substituents. However, both the compounds exist as monomers in a solution but dimeric in their solid states.[29] Later, Jutzi and his coworkers synthesized the first germylene, [(Me$_3$Si)$_3$C][(Me$_3$Si)$_2$CH]Ge: **17,** which exists as a stable monomeric form in both solution and solid state.[30] Furthermore, the silylene analogues of germanium such as unsaturated **18a-d**,[31]saturated **19a-d**,[32a] benzo-fused **20a-c**,[32b] *β*-diketiminate **21**[32c] and its chloro derivatives,[32d-e] and amidinate **22a-c**[32f-h] *etc*. were also reported and their derivatives of transition metals found

application in small molecules activation and catalysis. Kira et al. isolated the first cyclic dialkyl germylene **23** in 1999, which was analogous to Lappert's acyclic germylene.[33] In 1982, Veith and coworkers synthesized the four membered *N*-heterocyclic germylene, [$Me_2Si(NtBu)_2$]Ge: **24** and its tin and lead derivatives (Chart 2).

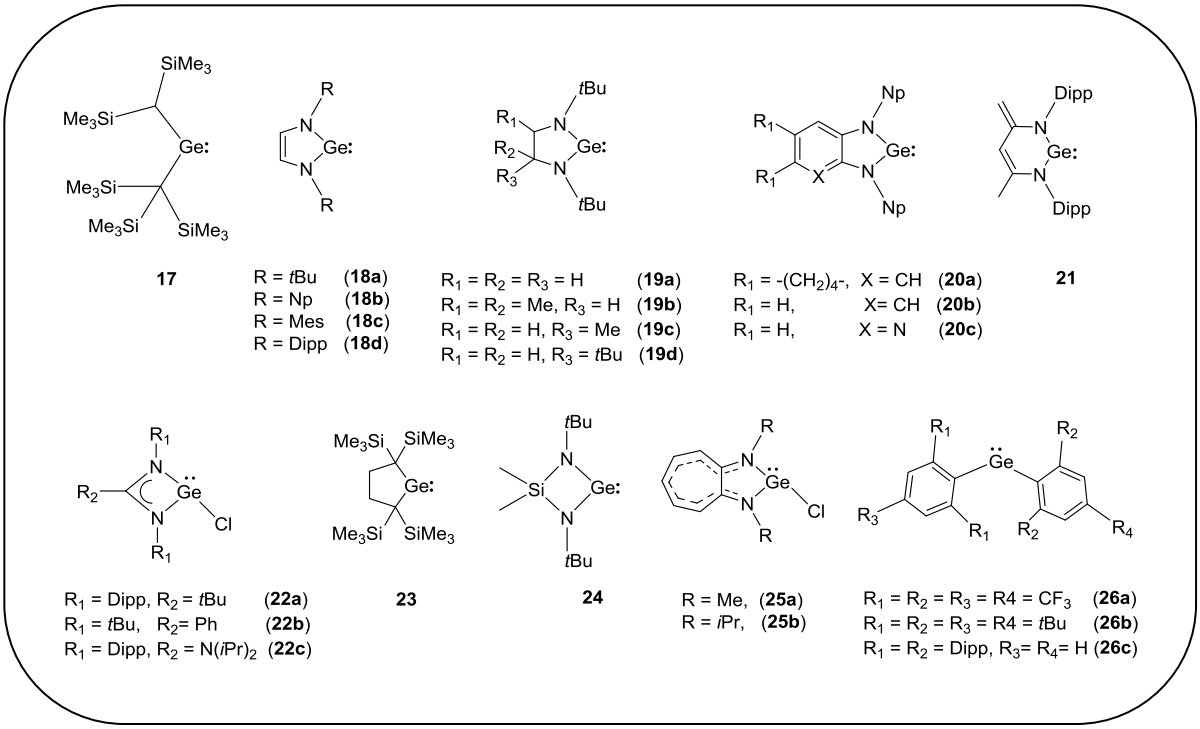


Chart 2. Selected examples of germylenes.

On the contrast, the respective silylene moiety was not synthesized till date due to instability of Si(II) center.[34] In recent years, the aminotroponiminate stabilized Ge(II) compounds **25a** and **25b** have been synthesized[35] and their derivatives have been applied in catalysis. In the following years, a variety of diaryl germylenes **26a-c** were also isolated by the various research group by using steric protection from suitable aromatic ligands.[36]

More recently, the germanium(II) cations have been realized by using neutral ligands.[37a] The monocations and dications of germanium are also unstable at ambient conditions due to its enormous electrophilicity of three vacant *p*-orbitals on the Ge(II) center.[37b] Such compounds generally possess two possible Lewis type models; (1) dative model and (2) more conventional covalent Lewis-type model as depicted in Figure 3.

In the case of Ge(II) dication, the Ge atom holds a lone pair of electrons and three vacant *p*-orbitals, unlike neutral germylenes (where Ge atom possesses a lone pair of electrons and one vacant *p*-orbital) and Ge(II) monocations (where Ge atom possesses a non bonding pair of electrons and two vacant *p*-orbitals).

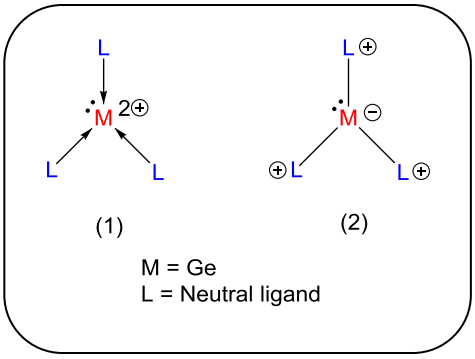


Figure 3. Lewis models for Ge^{2+} centers.

To make such species kinetically and thermodynamically stable for isolation, several methods have been designed with a variety of neutral ligands that could provide both donor capability as well as steric protection to the central atom. For example, neutral ligands are initially bound to the central atom, followed by reducing its electrophilicity through the transfer of lone pair into the empty *p*-orbitals of the central atom. Simultaneously the kinetic stabilization also provided by the bulky ligands that led to the isolation of such novel low-valent group 14 dications. Furthermore, the obtained cationic charge was also balanced by the surrounding weakly coordinating anions during the reaction (see in Chart 3).[37a]

In 2007, Baines and coworkers stabilized the first Ge(II) dication **27**[38] by using three strong σ-donor *N*-heterocyclic carbene ligands (NHC), where the dicationic charge was balanced by two weakly coordinating I^- anions (the closest Ge-I approach is 5.96 Å). The DFT calculations revealed that the charge on Ge(II) ion was actually delocalized onto the three NHCs ligands but not localized on the Ge(II) center. In the later case, Driess et al. used bis-NHC borate ligand that forms an unusual dinuclear $HGe:^{+}\rightarrow Ge:^{2+}$ cation **28**,[39] in which one germanium is monocationic and another is dicationic. Baines et al. in 2008 encapsulated the Ge(II) dication **29** by using an electron rich [2.2.2]-cryptand ligand,[40] where the six oxygen atoms in the ligand are effectively bound and the two nitrogen atoms are weakly coordinated to Ge center. However, the charge of the "naked" Ge(II) cation was balanced by two weakly coordinating triflate anions.

More recently, the research groups of Baines and Reid have demonstrated that the crown ethers are also suitable ligands to protect both Ge(II) mono and dications **30a-b,**[41] as well as their Lewis base derivatives of **31a-b** that is because of this unique structural characteristics of crown ethers.

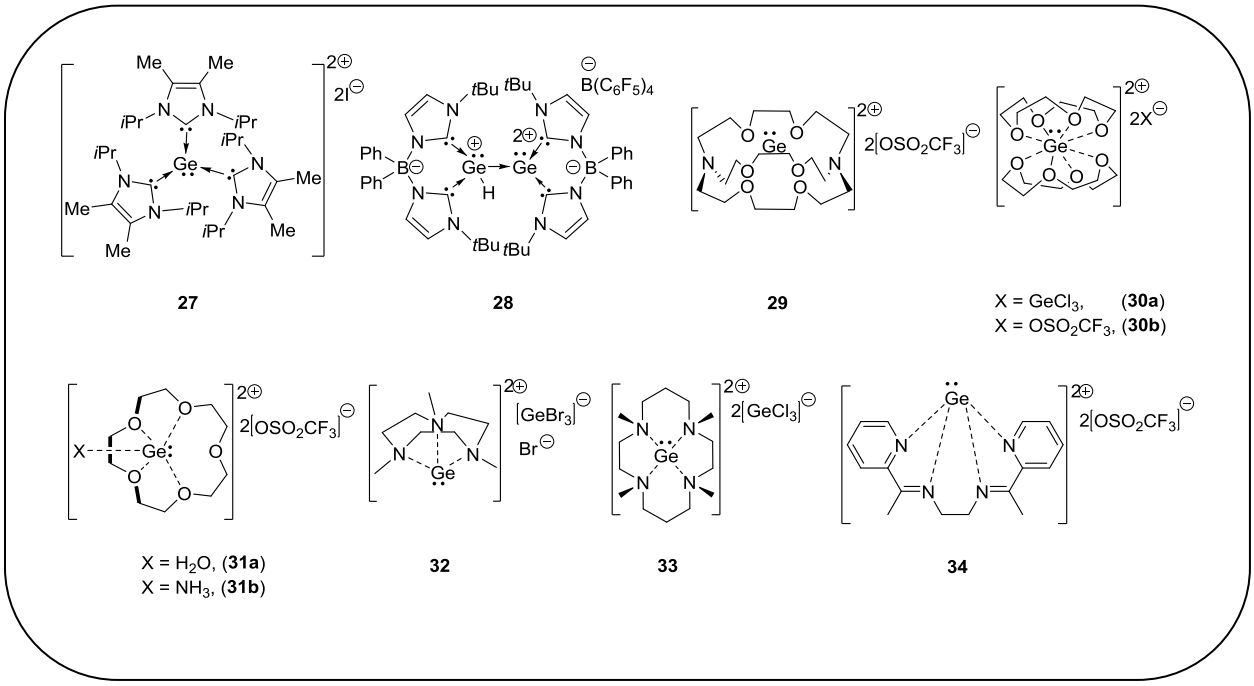


Chart 3. Selected examples of Ge(II) dications **27**-**34**.

This offered different structural models of Ge(II) dications which depends only on the correlation between the cavity size of the crown ether and ionic radii of Ge(II) moiety. Similarly, azamacrocycles such as tacn (1,4,7-triazacyclononane) and cyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) were utilized for the protection of Ge(II) dicationic centers **32** and **33**[42] adopting pyramidal and square antiprism sandwich structures, respectively. Braunschweig and coworkers recently introduced the MOLP concept (metal only Lewis pair) and stabilized the dication of tin and lead, but it is so far not extended for the Ge(II) dication isolation.[43] Very recently, the four coordinate Ge(II) dication **34** was reported by Majumdar et al. by the use of a 2,7-bis(2-pyridyl)-3,6-diazaocta-2,6-diene ligand (tetradentate). The Ge(II) dication further acts as a ligand for stabilizing the cationic transition metal complexes of Au(I) and Ag(I).[43f]

1.4. A Brief History of Small Molecule Activation, Especially H_2 and NH_3

The importance of small molecules like H_2, CO, CO_2, NH_3 is that they are ubiquitous, relatively inexpensive, synthons for constructing more complex molecules, and produced in large scales in industrial processes. Moreover, most of the homogeneous catalytic cycles involve such small molecules, like hydrogen, olefins, carbon monoxide and ammonia.[44]

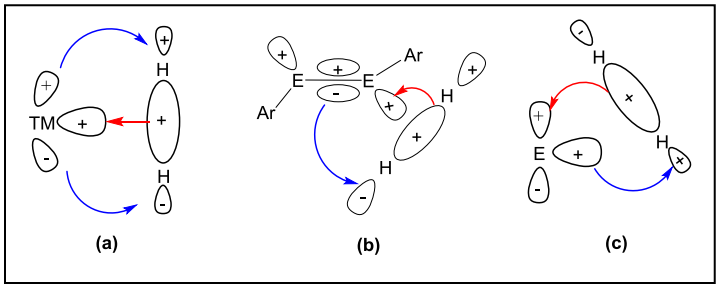
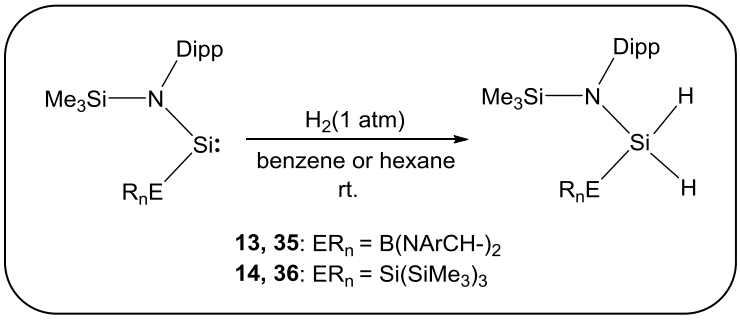


Figure 4. Frontier orbital interaction of dihydrogen with (a) transition metals, (b) main group multiple bonds, and (c) singlet main group species e. g. carbenes, tetrylenes.

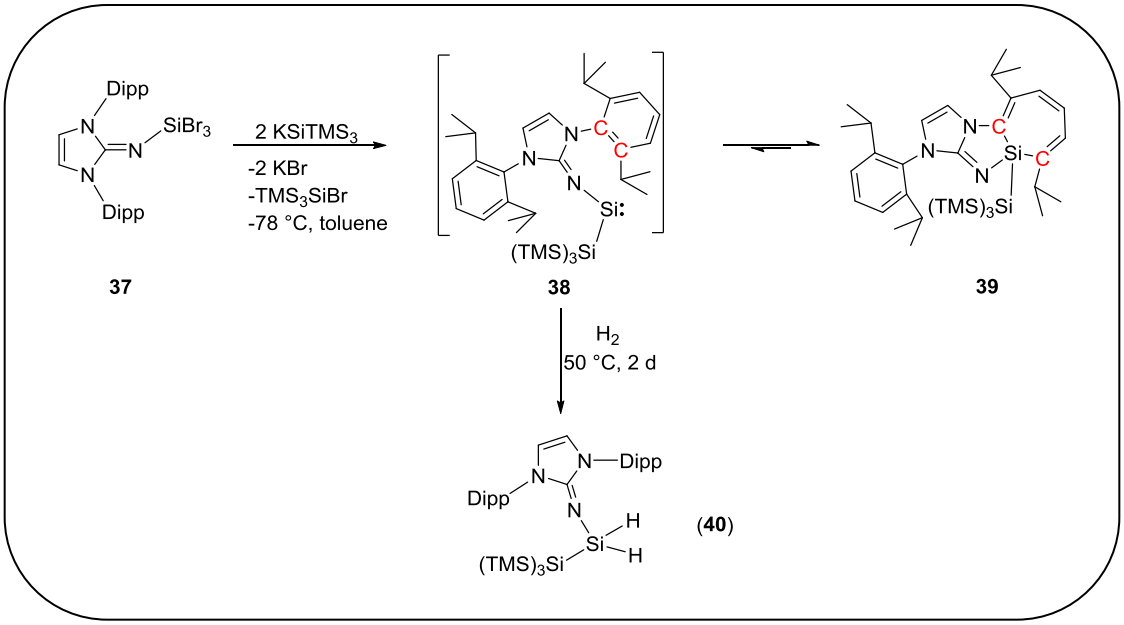
Can compounds with main group elements activate dihydrogen? The alkyne analogue of germanium [ArGe≡GeAr; Ar= 2,6-$Trip_2C_6H_3$ (Trip = 2,4,6-$i Pr_3C_6H_2$)] was demonstrated to react with H_2 under ambient conditions which yielded Ar(H)Ge=Ge(H)Ar, $Ar(H)_2Ge–Ge(H)_2Ar$ and $ArGeH_3$.[45] Bertrand and coworkers have shown that the reaction of an acyclic alkyl amino carbenes (aAAC) [C(*t*Bu)N*i*Pr_2] with H_2 led to the splitting of the dihydrogen bond and formation of H_2C(*t*Bu)N*i*Pr_2.[46] Detailed theoretical investigations revealed that the initial step is the donation from the lone pair or pi-electron of carbene or digermyne to the σ* orbital of H_2 with concomitant electron donation from the σ-orbital of H_2 to LUMO of carbene and digermyne (Figure 4) These studies unravel a fundamental mode of reactivity which is prototypical for late transition metals was unfolded for low valent main group elements.



Scheme 2. Activation of H_2 by acyclic silylenes **13** and **14**.

Very recently, Aldridge, Jones, and Mountford have synthesized two stable acyclic silylenes (i) a stable mixed (amido) boryl silylene (**13**), Si{B(NDippCH)$_2$}{N(SiMe$_3$)Dipp} (Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$) and (ii) the silyl coordinated silylene (**14**), Si{Si(SiMe$_3$)$_3$}{N(SiMe$_3$)Dipp}, which were found to split dihydrogen and afford the corresponding dihydrosilanes, H$_2$Si(B(NArCH–)$_2$)(N(SiMe$_3$)Dipp) **35** and H$_2$Si(Si(SiMe$_3$)$_3$)(N(SiMe$_3$)Dipp) **36**, respectively (Scheme 2).[26]

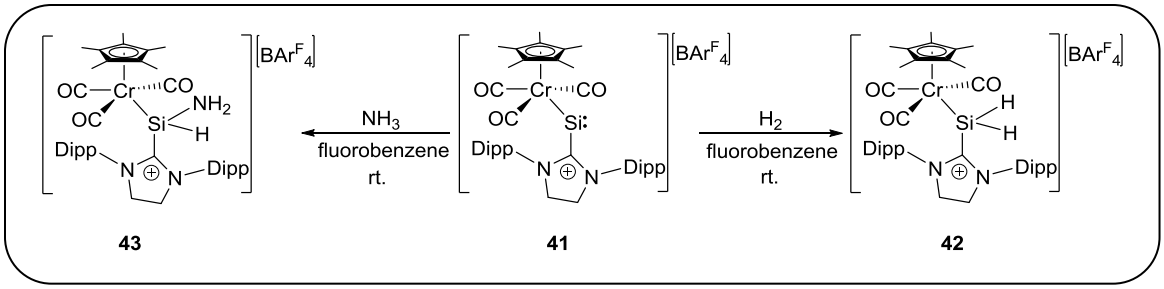
Inoue and his coworkers recently reported the *in situ* generated iminosupersilylsilylene **38** from tribromosilane derivative **37**, which was equilibrium with a formal Si(IV) compound, namely 'silepin' **39** serving as a masked silylene. Experimental and computational studies revealed that the equilibrium between **38** and **39** was thermally accessible. The subsequent reactivity of **38** with dihydrogen afforded the corresponding activation product **40** shown in scheme 3.[47]



Scheme 3. Synthesis of masked silylene and its H_2 activation.

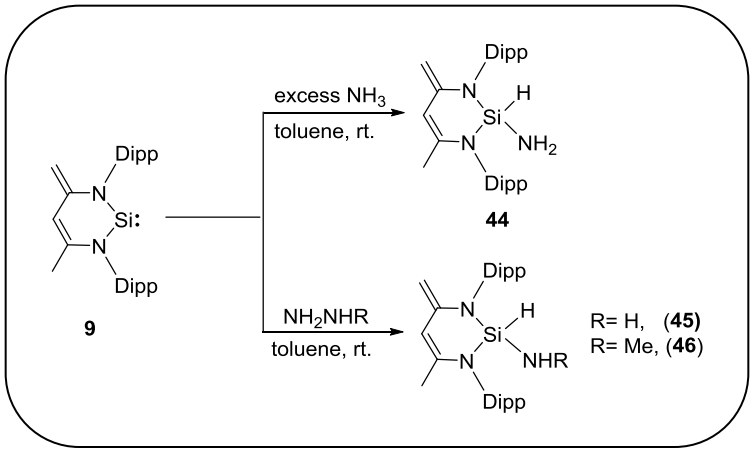
Recently, a stable NHC-supported cationic metallasilylene **41** was synthesized by Filippou et al. (Scheme 4).[48] **41** enables the activation of dihydrogen and ammonia, forming the corresponding derivatives of NHC-ligated silylium ions **42** and **43**, respectively. Utilizing a zwitter-ionic NacNac'Si **9** for activation of ammonia, Roesky and co-workers described the formation of a 1,1-addition product, NacNac'SiH(NH$_2$) **44**.[49a] Sicilia and coworkers calculated

the reaction of **9** with NH_3 computationally and observed that the formation of 1,4-addition product, which is kinetically and thermodynamically more favorable than the 1,1-addition product [48.7 kcal/mol (for 1,1-addition product) *vs* 26.6 kcal/mol (1,4-addition product)].[49b]



Scheme 4. Activations of H_2 and NH_3 with metallasilylene **41.**

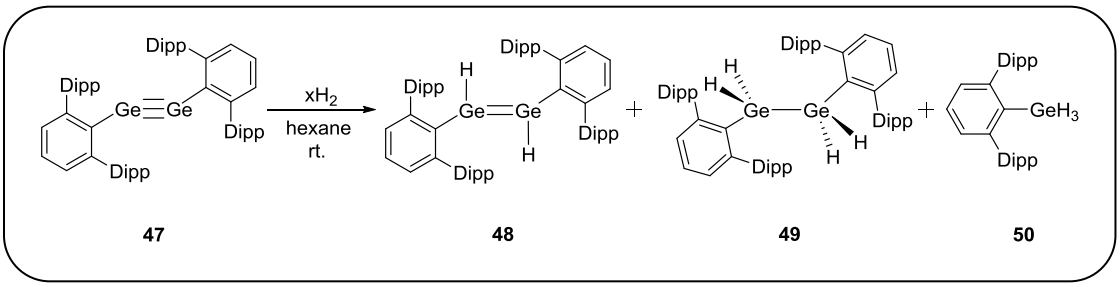
Sicilia and coworkers calculated the reaction of **9** with NH_3 computationally and observed that the formation of 1,4-addition product, which is kinetically and thermodynamically more favorable than the 1,1-addition product [48.7 kcal/mol (for 1,1-addition product) *vs* 26.6 kcal/mol (1,4-addition product)].[49b] However, when the free-energy profiles were calculated for the reaction of **9** with two equivalents of NH_3 (because Roesky et al. used an excess of NH_3), there is a significant decrease of the energy barrier for the 1,1-addition product (15.3 kcal/mol) and thus permitting its formation.[49a] In a subsequent report, the analogous cleavages of the N–H bond in hydrazine and N-methyl hydrazine were demonstrated by Roesky et al. with **9,** resulting in the corresponding 1,1-addition products **45** and **46** (Scheme 5).[49c]



Scheme 5. Activation of ammonia and hydrazines with **9**.

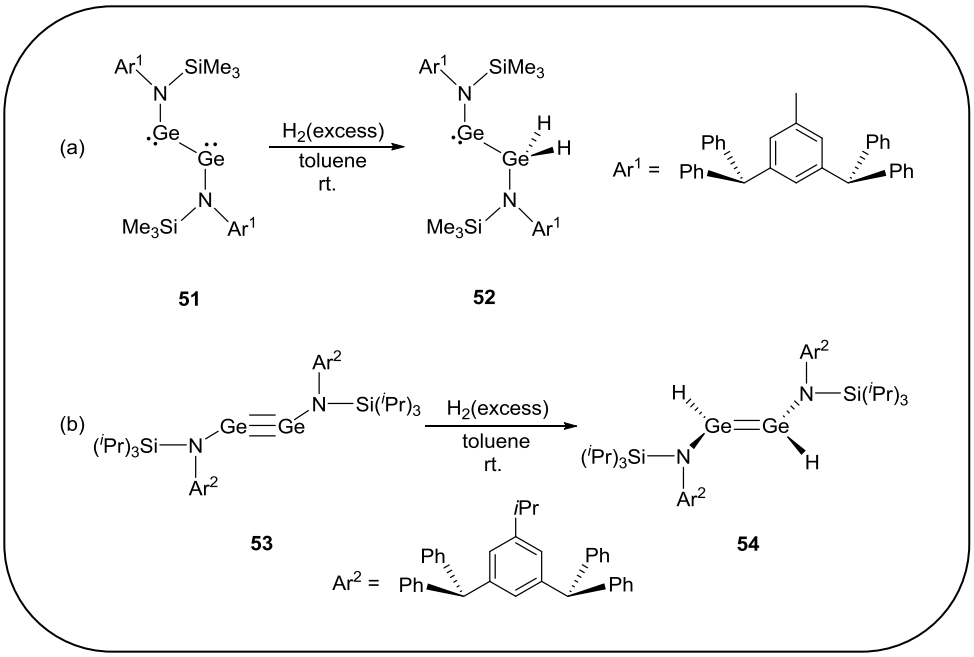
Driess and coworkers also isolated the adduct of **9** with $Ni(CO)_3$, which readily reacts with ammonia, isopropylamine, and phenylhydrazine in a 1,4-fashion giving rise to the corresponding

NacNac'Si(II)–$Ni(CO)_3$ complexes. Surprisingly, the adduct of **9** with $Ni(CO)_3$ showed 1,4-addition without rupturing the Si-Ni bond or ligand exchange at the Ni(0) center.[50] Power and coworkers in 2005 observed the activation of H_2 with the alkyne analogue of germanium, $Ar^{iPr4}Ge{\equiv}GeAr^{iPr4}$ (Ar^{iPr4} = 2,6-(2,6-*i*Pr_2-C_6H_3)$_2$-C_6H_3) **47**, afforded a mixture of a "digermene", a digermane, and a primary germane (**48** to **50,** Scheme 6)[45].



Scheme 6. Dihydrogen activation by a digermyne **47**.

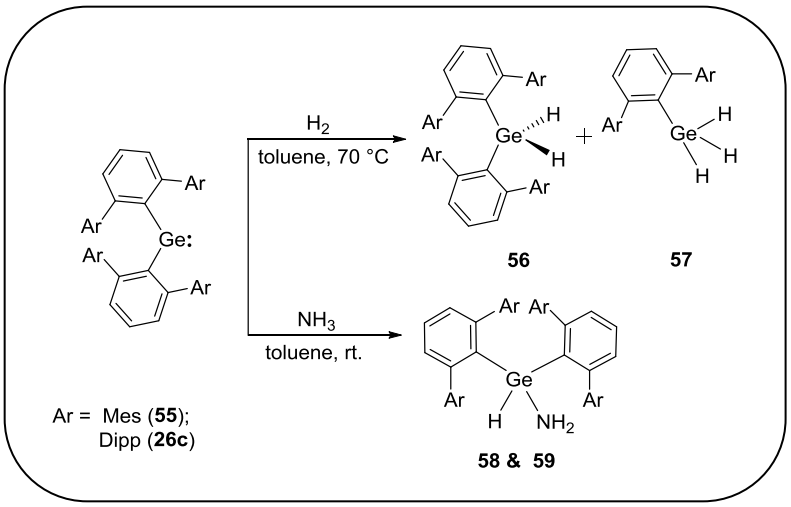
Later, Jones and coworkers expanded the splitting of dihydrogen by alkyne analogue of germanium by employing an amido-digermyne [(Ar^1)($SiMe_3$)NGeGeN(Ar^1)($SiMe_3$)] **51** (Ar^1=2,6-[C(H)Ph_2]$_2$-4-MeC_6H_2) for dihydrogen activation.



Scheme 7. Dihydrogen activation by (a) an inter-connected bis-germylene and (b) an amido-digermyne.

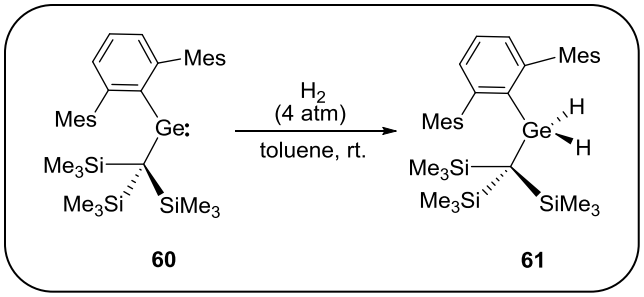
Unlike Power's digermyne, Jones' compound possesses a Ge–Ge single bond, so better to be referred to a bis-germylene.[51a] The reaction of **51** with dihydrogen forms a stable asymmetric monohydrogenation product$(Ar^1)(SiMe_3)NGeGe(H_2)N(Ar^1)(SiMe_3)$ **52** at room temperature (Scheme 7). Unlike **47**, compound **51** did not get activate by further equivalents of dihydrogen even upon heating up to 100 °C. Computational studies by Frenking et al.[51b] showed that the initial addition of H_2 to **51** forms the singly bridged hydride species $(Ar^1)(SiMe_3)NGeGe(H_2)N(Ar^1)(SiMe_3)$, which follows a low activation pathway and forms the most stable isomer **52**. However, the second equivalent of H_2 leading to the formation of $(Ar^1)(SiMe_3)NGeH$ and $(Ar^1)(SiMe_3)N\ GeH_3$. By utilizing the steric bulkiness on the amido ligand, the same group reported the amido-digermyne $[(Ar^2)(Si\textit{i}Pr_3)NGeGeN(Ar^2)(Si\textit{i}Pr_3)]$ (**53**; Ar^2 = 2,6-$[C(H)Ph_2]_2$-4-*i*PrC_6H_2) that features a Ge–Ge multiple bond. This is attributed to the smaller HOMO-LUMO gap (0.79 eV). **53** also reacts with dihydrogen and generate the corresponding hydrido-digermene $[(Ar^2)(Si\textit{i}Pr_3)NGe(H)Ge(H)N(Ar^2)(Si\textit{i}Pr_3)]$ **54** (Scheme 7).[52] Similar to compound **47**, the formation of di- or tri-hydrogenation products were not observed even with excess H_2 at higher temperature.

In 2009, Power and co-workers used extremely bulky divalent two-coordinate germylenes $(ArMe^6)_2Ge$: **55** ($ArMe^6$ =2,6(2,4,6-Me_3-$C_6H_2)_2$-C_6H_3) and $(Ar^{\textit{i}}Pr_4)_2Ge$: **26c** (Ar*i*$Pr_4$ =2,6-(2,6-*i*Pr_2-$C_6H_3)_2$-C_6H_3) for dihydrogen activation and observed the formation of corresponding hydrogenated products $(ArMe^6)_2GeH_2$ **56** and (Ar*i*Pr_4)GeH_3 **57** along with the formation of HArDipp (Scheme 8).[53a]



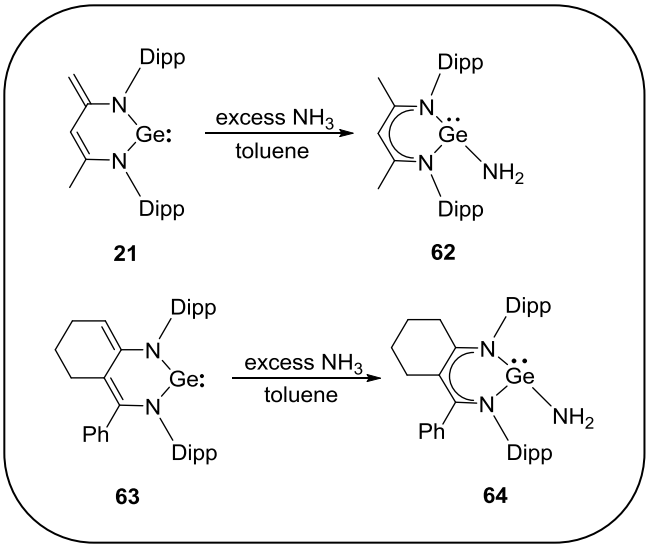
Scheme 8. Reactions of H_2 and NH_3 with diaryl germylenes.

The analogous reactions of **55** and **26c** with NH_3 exclusively yielded $(ArMe^6)_2Ge(H)(NH_2)$ **58** and $(Ari Pr_4)_2Ge(H)(NH_2)$ **59** at room temperature.[53a] Recently, Aldridge and co-workers have accomplished the oxidative addition of H_2 by utilizing the aryl silyl germylene **60**, resulting the dihydride product **61** (Scheme 9).[53b] Similar to compound **9**, the NacNac'Ge **21** also reacts with ammonia at room temperature to give the 1,4-addition product **62**.



Scheme 9. Reactions of NH_3 with diaryl germylene **60**.

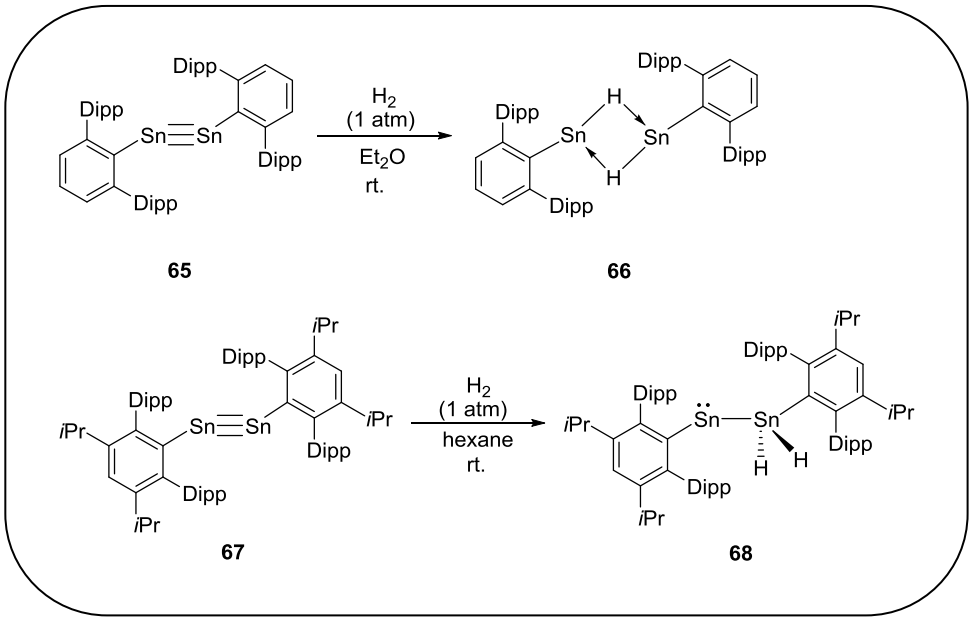
DFT calculations revealed that the 1,4-addition product was kinetically and thermodynamically more stable than 1,1 addition product by 13.6 kcalmol^{-1}.[49b]



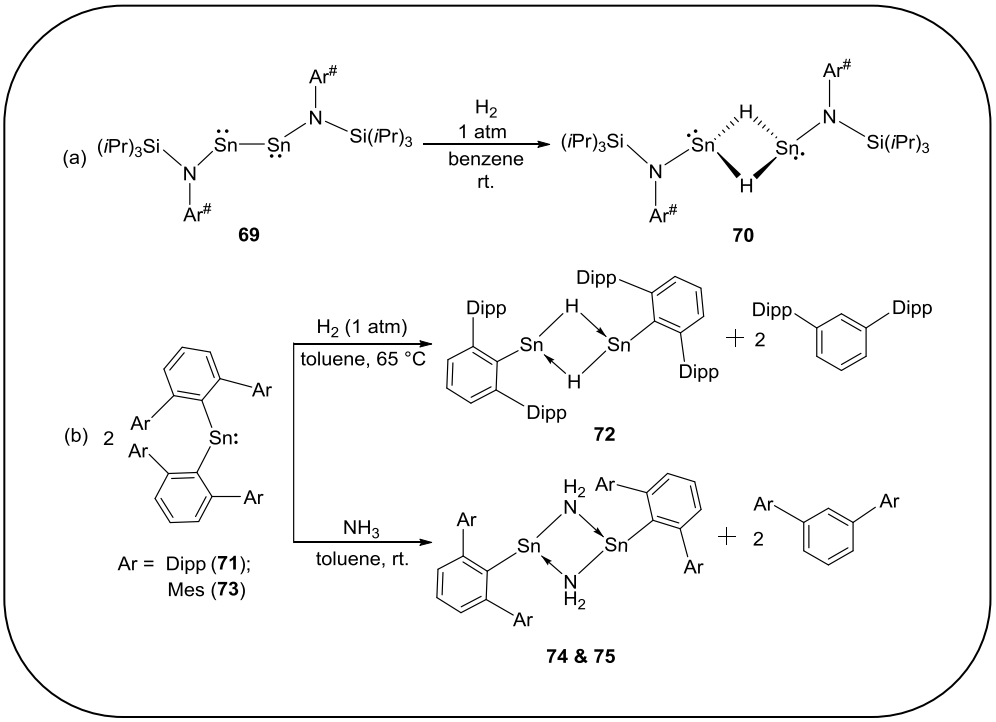
Scheme 10. Ammonia activation by a *N*-heterocyclic germylenes **21** and **73**.

Later, Driess and coworkers prepared a similar zwitterionic *N*-heterocyclic germylene **63** which also reacts with NH_3 to yield the 1,4-addition product **64** (Scheme 10).[54] Similar to digermyne, distannynes are also capable of activating dihydrogen. The tin analogues of ArDippSnSnArDipp **65** and ArDipp*SnSnArDipp* **67** [ArDipp* = 2,6-(2,4,6-$i Pr_3C_6H_2)_2$-3,5-

*i*Pr$_2$-C$_6$H)] enabled the formation of symmetrically bridged Sn(II) hydrides, ArDippSn(μ-H)$_2$SnArDipp **66** and ArDipp*SnSn(H$_2$)ArDipp* **68** (Scheme 11).



Scheme 11. Activation of dihydrogen by distannynes **65** and **67**.

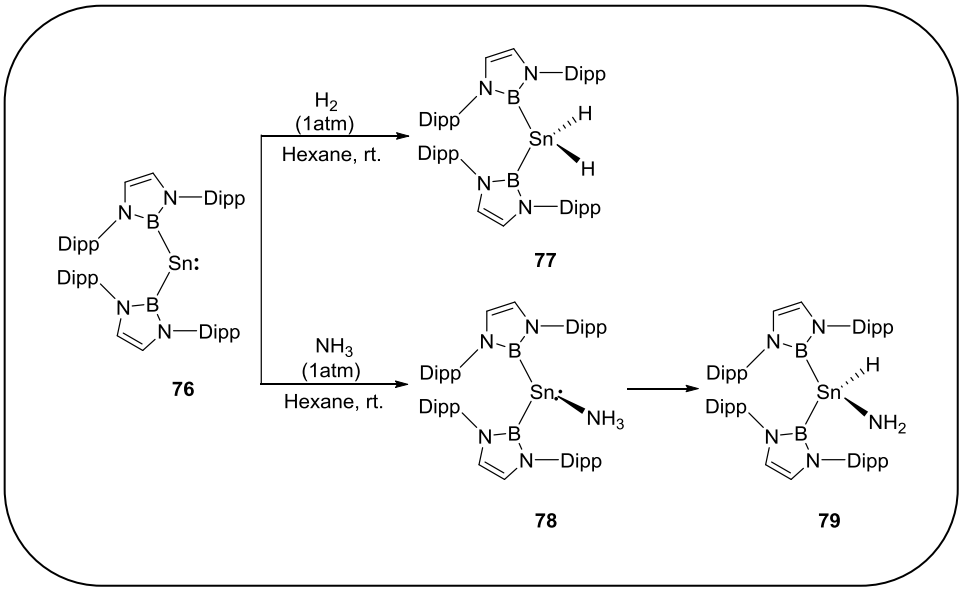


Scheme 12. (a) Activation of H_2 by a distannyne. (b) Activations of H_2 and NH_3 by stannylenes.

Jones and coworkers have recently isolated a distannyne $Ar^{\#}SnSnAr^{\#}$ **69** ($Ar^{\#}$= 2,6-(2,4,6-*i*Pr_3-C_6H_2)$_2$-3,5-*i*Pr_2-C_6H) by using a sterically bulky amido ligand, which could also activate the dihydrogen to give $Ar^{\#}Sn(\mu\text{-}H)_2Sn\ Ar^{\#}$ **70**.[55]

Unlike germylenes, stannylenes afford the symmetrically bridged Sn(II) hydride $(Ar^{Dipp}Sn(\mu\text{-}H))_2$ **72** from the reaction of $SnAr^{Dipp2}$ **71** with H_2 but no reaction took place with $SnAr^{Mes2}$ even at elevated temperatures (70 °C). Similarly, the diaryl stannylenes **71** and **73** could also activate NH_3 to yield the corresponding amido bridged complexes $Ar^{Dipp}Sn(\mu\text{-}NH_2)_2SnAr^{Dipp}$ **74** $Ar^{Mes}Sn(\mu\text{-}NH_2)_2SnAr^{Mes}$ **75**, respectively (Scheme 12).[56]

Very recently, the groups of Aldridge, Jones, and Mountford demonstrated the reaction of H_2 with bis(boryl) stannylene complex $Sn(B(NArCH)_2)_2$, **76**, which forms the corresponding Sn(IV) product (**77**). This represents the first example of simple oxidative addition of H_2 with a monometallic Sn(II) system to generate a Sn(IV) product. Similarly, the activation of ammonia with **76** proceeds *via* an ammonia adduct **78,** which finally results in the formation of amidotin(IV) hydride **79** (Scheme 13).[57]

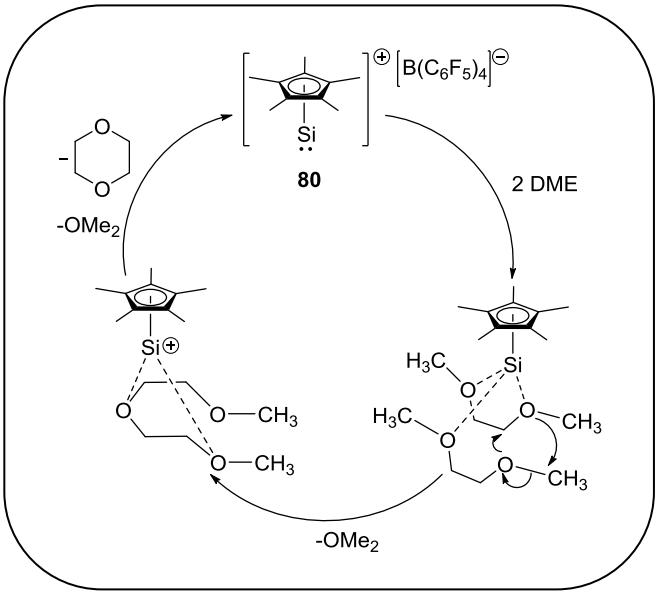


Scheme 13. Activations of H_2 and NH_3 by bis(boryl) stannylene.

1.5. Compounds with Heavier Main Group 14 Elements in Homogeneous Catalysis

Inspite of silylene supported transition metal systems, the designing of new group 14 based catalytic system devoid of any transition metals has been attracting the attention of current research.

Unlike FLP based systems,[58] which has undergone remarkable progress in recent years, catalysis with a single component main group system has been less explored. The seminal review by Power, in nature motivated the chemists across the world to explore catalysis with main group compounds.[59] The central dogma behind this interest is the availability of lone pair as well as a vacant *p* orbital in the subvalent main group compounds, a description more common for transition metals. The groups of Roesky and Baceiredo have demonstrated the stoichiometric conversions of CO_2 to methanol and hydrosilylation of olefins by using Nacnac Ge(II) and Si(II) hydrides, respectively.[60] However, in both of these studies, they could not propose the catalytic cycle. The study of compounds featuring low valent main group elements continues to be a worthwhile subject due to their anticipated application in metal free catalysis.

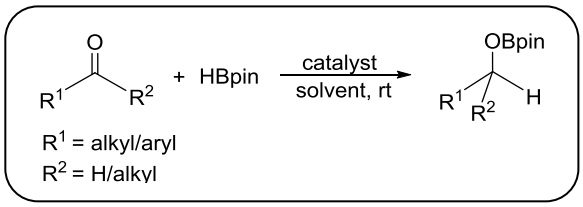


Scheme 14. Si(II) cation catalyzed DME to 1,4-dioxane.

Recently, **80** has been found to catalytically convert 1,2-dimethoxyethane (DME) to 1,4-dioxane and dimethyl ether (Scheme 14), which is a rare example of a transition metal free catalytic transformation.[37b],[61] Ab initio calculation indicates that the O→Si dative bond in the DME→**80** complex is electrostatic in nature and the subsequent enhancement of positive charge at the Si(II) center facilitates the attack of another equivalent of DME. This catalytic process is detected to be useful for a range of oligo(ethylene glycol)diethers, leading to 1,4-dioxane and dimethyl ether in each case.

1.5.1. Hydroboration

The hydroboration is an important tool for the reduction of carbonyl compounds to alcohols (Scheme 15), which has emerged as a prevailing strategy for advanced organic synthesis in both academic and industrial laboratories.



Scheme 15. Hydroboration of carbonyl compounds with HBpin.

The hydroboration is an important tool for the reduction of carbonyl compounds to alcohols (Scheme 15), which has emerged as a prevailing strategy for advanced organic synthesis in both academic and industrial laboratories. Despite the transition metal catalysts,[62] a metal-free oxazaborolidine was demonstrated as an enantioselective hydroboration catalyst by Corey and coworkers in 1987.[63] Later on, Woodward et al. also described an enantioselective reduction of ketones using a chiral Ga complex in 2000.[64]

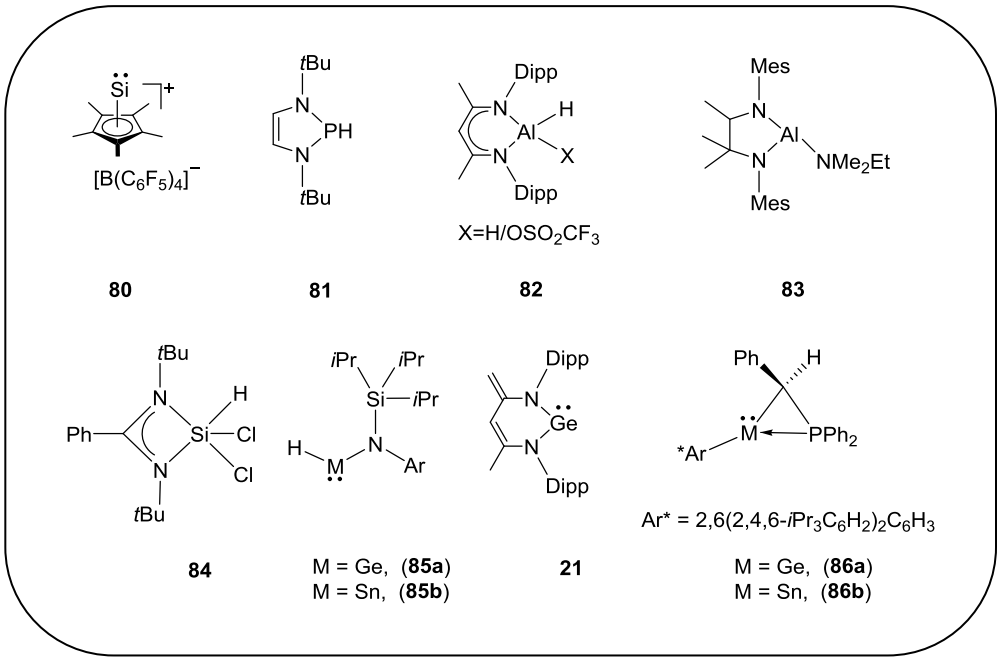


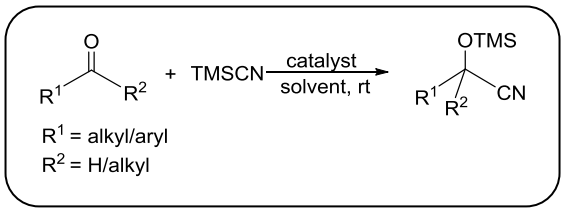
Chart 4. Selected examples of hydroboration catalysts with *p*-block elements.

The groups of Kinjo (**81**), Roesky (**82**), Nebenna (**83**), and Our group (**84**) recently developed the main-group hydroboration catalysts based on phosphorus, aluminium, and silicon hydrides.[65] The selective examples these catalysts (**80-86** and **21**) are given in Chart 4.

Based on the theoretical inputs given by Takagi and Sakaki, the divalent Ge(II) and Sn(II) hydrides [2,6-$(CHPh_2)_2$-4-*i*Pr-$C_6H_2(SiMe_3)$N-M(H) (M = Ge and Sn)] **85a-b** reported by Jones et al. were found to be efficient catalysts (optimal reaction conditions; 0.05-2.5 mol%, 0.17-168 h) for the hydroboration of a variety of unactivated carbonyl compounds.[65b] Later on, Zhao et al. reported *N*-heterocyclic ylide-like germylene **21** for the hydroboration of carbonyl compounds (optimal reaction conditions; 2 mol%, 24 h).[66] The intramolecular Lewis pairs of germylene **86a** and stannylene **86b** have also been distinctly examined by Wesemann's group for the hydroboration of aldehydes and ketones at room temperature (optimal reaction conditions; 0.1 mol%, 30 min).[67]

1.5.2. Cyanosilylation

The cyanosilylation of carbonyl compounds is a versatile protocol for the C–C bond formation and protection of the alcohol functionality (Scheme 16). The compounds with main group elements[68], transition metals[69], and lanthanides[70] have been utilized as catalysts for the preparation of cyanohydrins to develop various significant compounds with medicinal applications, such as α-hydroxy acids, α-hydroxy ketones, α-amino acids, and *β*-amino alcohols[71].



Scheme 16. Cyanosilylation of carbonyl compounds with TMSCN.

Cyanosilylation was first studied by Winkler using hydrogen cyanide (HCN) as a cyanide source[72]. Parallel to this work, several methods were established with safer alternative cyanating agents to avoid the poisonous HCN. At the earlier stage, the group of Shibasaki introduced a new bifunctional asymmetric aluminum catalyst **87** for cyanosilylation of aldehydes at ambient conditions. This catalyst contains both the Lewis acid and base moieties, where the aluminium can work as Lewis acid to activate the carbonyl group, while the oxygen atom of the phosphine oxide can act as Lewis base

to activate the silylated nucleophiles.[73] Recently, the groups of Roesky[68d] and Nagendran[74] reported aluminum based catalysts (**88** and **82**) for cyanosilylation of carbonyl compounds, respectively, giving good to excellent yield.

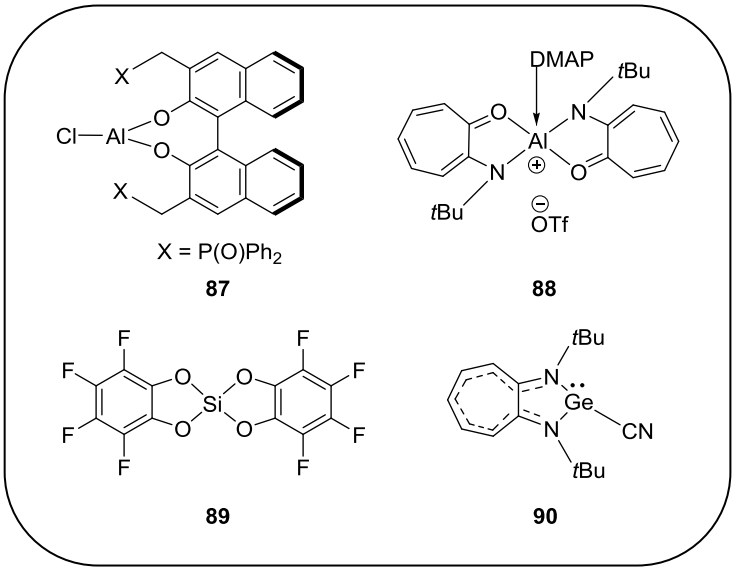
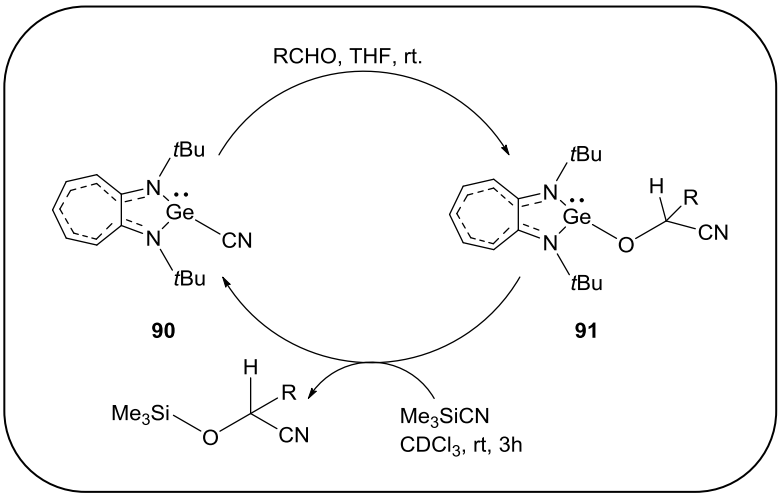


Chart 5. Selective examples of cyanosilylation catalysts with *p*-block elements.

Bergman and Tilley have demonstrated the cyanosilylation of 4-nitro-benzaldehyde with bis(perfluorocatecholato)silane [Si(cat^{F})$_2$] **89**.[68e] So far, the heavier *p*-block catalysts with regular oxidation state have been explored for carbonyl cyanosilylation. Interestingly, there is only one example of a three coordinate germanium (II) cyanide [LGeCN] (L= aminotroponiminate) **90** as a catalyst for aldehyde cyanosilylation under mild reaction conditions (Chart 5).



Scheme 17. Cyanosilylation of aldehydes and proposed catalytic cycle.

The catalytic cycle initially proceeds through a stoichiometric reaction of **90** with aldehydes to give the corresponding alkoxide derivatives **91**. It further undergoes σ–bond metathesis with TMSCN and formed the final cyanosilylated product in moderate to good yield (Scheme 17).

1.6. Scope and Objectives of the Thesis Work

The syntheses of heavier group 14 element compounds in low oxidation state are an emerging domain due to their unique electronic properties. Unlike saturated compounds, the central atom in these compounds possesses a vacant orbital and a pair of electrons in their valance shell. In order to explore such compounds, the selection of a suitable ligand is indeed an art in main group chemistry because the usage of bulky ligands, with appropriate steric and electronic effects, is an essential factor. Several ligands were showed to be very efficient in this perspective and already reported by different groups. For example Roesky and coworkers has already studied the chemistry of Al(I), Ge(II) and Sn(II) with the support of sterically bulky *β*-diketiminato ligand HC(CMeNAr)$_2$ (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$). Recently Driess et al. also isolated silylene with the use of this ligand. In view of these literature surveys, amidinate system with appropriate steric and electronic protection is suitable for the isolation of main group compounds in low oxidation state. This is attributed to the following properties of amidinate ligand (see in Figure 5).

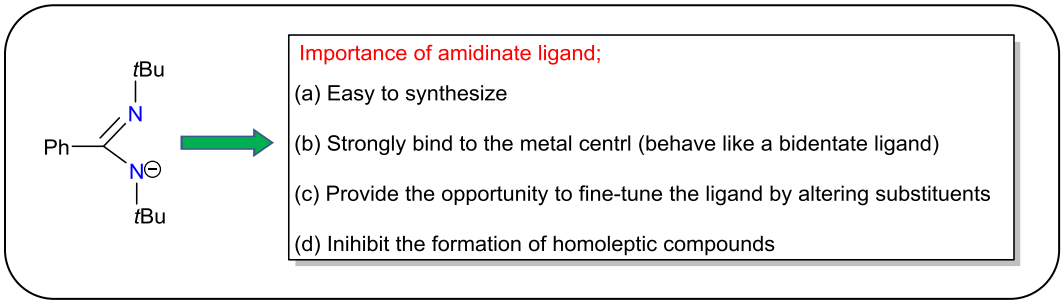
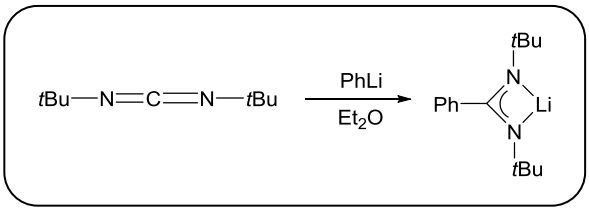


Figure 5. Structural representation of amidinato ligand.

The major advantage of using amidinato ligands is that their steric and electronic properties can be altered through variation of the substituents on the nitrogen and carbon atoms. Due to the geometric restraints of the NCN ligand backbone, amidinates have small N–M–N bite angles (generally 63–65°), and provides both chelating and bridging coordination modes with the metal center. Moreover, the substituents on the nitrogen atoms of on the amidinato can be employed for tuning the steric requirement of the ligand, that determines the coordination geometry at the metal center. Roesky et al. reported the first heteroleptic chloro silylene (**10a**) by the support of amidinato ligand using *t*Bu

substituents on nitrogen atoms.[23a] Benzamidinate supported complexes (nickel, vanadium, and yttrium) have already been investigated for catalytic reactivity, and it has been found that the ligand is attractive towards catalysis. So we selected amidinato ligand, judiciously and prepared both usual and subvalent compounds of silicon. The preparation of amidinate ligand was very straightforward. The *tert*-butylcarbodiimide reacts with one equivalent of PhLi in diethyl ether gives rise to the amidinato lithium (Scheme 18).[23a] Si(II) and Si(IV) chemistry of the support of benzamidinato ligand are briefly discussed in this thesis.

By using the advantages of amidinato-ligand, our group synthesized a neutral penta coordinate Si(IV) compound and three coordinate silylene [PhC(N*t*Bu)$_2$SiN(SiMe$_3$)$_2$] in C-F, B-H and C-H bond activations. These results inspired to use as single-site hydroboration catalyst.



Scheme 18. Synthesis of amidinato lithium.

On the other hand, the low-valent chemistry of germanium is also stabilized by neutral ligands and results in the formation of Ge(II) mono and dications. Considering the unique electronic properties of isocyanide ligand, for the first time introduced as neutral donor ligand to isolate such cations because isocyanide is a strong σ-donor and weak π-acceptor than CO. It also forms the metal carbene type bond like NHC carbene.

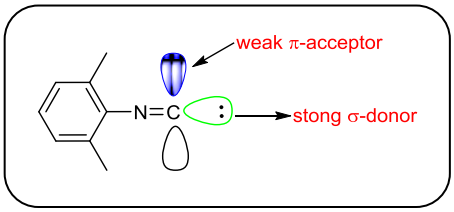


Figure 6. Structural representation of isocyanide ligand.

Therefore, the purpose of this thesis work is to study the synthesis, reactivity and catalytic application of low-valent group 14 element compounds.

1.7. Organization of the Thesis

The thesis is divided into five chapters.

Chapter-1 provides brief introduction to low-valent chemistry of heavier group 14 compounds, small molecule activation, and their catalytic application in homogeneous catalysis.

Chapter-2 describes the use of the isonitrile as a ligand for stabilizing the Ge(II) dication $[(RNC)_4Ge:]_2^{+}[:GeCl_3]_2^{-}$. The reaction occurs in a single step. The compound was fully characterized by using state of the art spectroscopic tools as well as single crystal X-ray study. Furthermore, NBO analysis was described to understand the nature of bonding in these complexes.

Chapter-3 illustrates the activation of C(sp^3)-H and C-F bond of respective acetophenone and 1,1,1 trifluoroacetophenone by thermally stable silylene, $[PhC(N\textit{t}Bu)_2SiN(SiMe_3)_2]$ at ambient conditions. Full quantum chemical calculations were done to understand the mechanism, which indicates the reaction is both kinetically and thermodynamically feasible at room temperature.The scope of C-F bond activation was further extended with C_6F_6 and $C_6F_5CF_3$.

Chapter-4 describes the synthesis and characterization of a new benz-amidinato silane, $[PhC(N\textit{t}Bu)_2SiH(Me)Cl]$ and its application as a catalyst for cyanosilylation of aldehydes. This is the first example of a neutral penta-coordinated Si(IV) species that catalyses cyanosilylation of a variety of aromatic and aliphatic aldehydes under mild reaction conditions in good yields. A plausible mechanism for this cyanosilylation of aldehydes has been given with the isolation of a key intermediate.

Chapter-5 describes the reactivity of silicon(II) compound $[PhC(N\textit{t}Bu)_2SiN(SiMe_3)_2]$ with pinacolborane and aldehyde at room temperature. At the outset, we have performed the reactions of $[PhC(N\textit{t}Bu)_2SiN(SiMe_3)_2]$ with HBpin and aldehydes. Subsequently, we have used the silylene as a catalyst for the hydroboration as well as for cyanosilylation of aldehydes and ketones. This is, to our knowledge, the first report of a Si(II) compound as a single-site catalyst. In order to gain more insight about the mechanism, we have performed stiochiometic reactions that results in the isolation of one of the key intermediates and the obtained intermediate was characterized by single crystal X-ray diffraction studies and multi-nuclear NMR spectroscopy.

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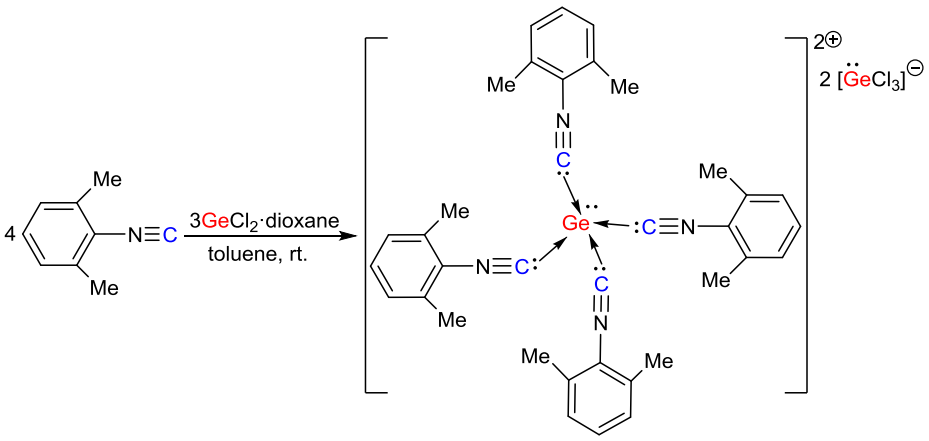
Synthesis of a Ge(II) Dication by Using Isocyanide Ligands



Abstract

Herein, we introduce isocyanide as a ligand in main group chemistry and describe the facile isolation of a Ge(II) dication. The reaction of 2, 6-dimethylphenylisocyanide with $GeCl_2$ leads to the formation of a Ge(II) dication with two $[GeCl_3]^-$ molecules as counter anions. The dicationic Ge(II) center is bound to four isocyanide ligands and also holds a lone pair of electrons. DFT calculations revealed that the dication is stabilized only by σ-donation from the four isocyanide ligands. Natural population analysis gives a charge of +0.74 on the Ge(II) center, indicating that the positive charge is shared by the isocyanide substituents.

2.1. Introduction

The bonding depiction of Ge(II) dications is very interesting. The central germanium atom holds a lone pair of electrons and three unoccupied valance *p*-orbitals. In contrast to neutral germylenes[1] and Ge(II) monocations,[2] in which the valence electron counts are six and four, respectively, the valence electrons in the Ge(II) dications is only two. Consequently, the isolation of such dications at ambient conditions is difficult. Understandably, the number of Ge(II) dications that have been prepared so far is very limited (Chart 1).There are primarily two synthetic strategies that have been utilized for isolating Ge(II) dications: (a) the use of a N-heterocyclic carbene (NHC) **1**[3] and bis-carbene **2**[4] and (b) encapsulation of Ge(II) dications in macrocycles like cryptand **3**, crown ethers **4**, and azamacrocycles **5**.[5–8]

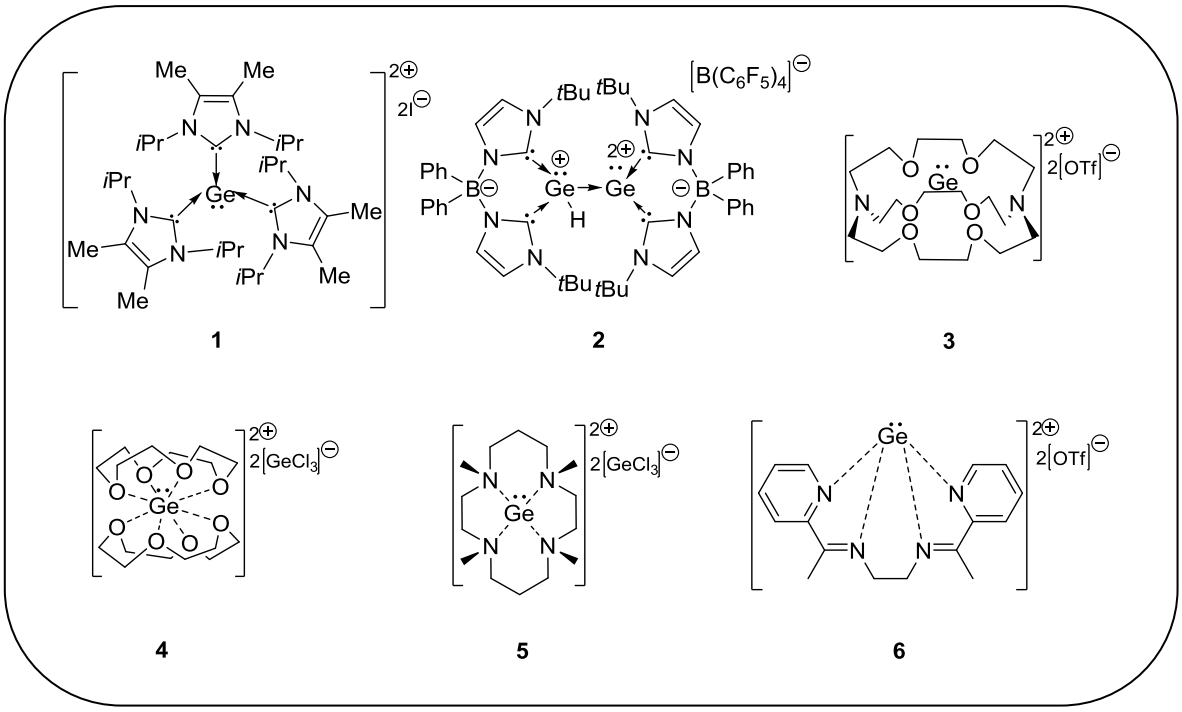


Chart 1. Selected examples of Ge(II) dications.

In case of N-heterocyclic carbene (NHC) stabilized Ge(II) dication **1**, the Ge(II) center is bound to three equivalent NHC carbene ligands and the dicatonic positive charge was balanced with aid of two non coordinating iodide anions. Later, Driess and coworkers isolated the Ge(II) dication **2** by employing Bis-NHC borate ligand. In 2008, Baines' group encapsulated the Ge(II) dication **3** by the use of electron rich [2.2.2] cryptand ligand, in which, the compound showed minimal interaction between the Ge(II) dicationic center and two triflate anions. Recently, the research groups of Baines and Reid have demonstrated that crown ethers are also fitting ligands for the stabilization of Ge(II) dications by isolating a

$[Ge([12]crown\text{-}4)_2][GeCl_3]_2$ **4**, where two of [12]crown-4 molecules sandwiching a Ge(II) center and two $[GeCl_3]$ counter anions were clearly separated from the Ge^{2+} center. Utilizing Me_3-tacn (1,4,7-trimethyl-1,4,7-triazacyclononane) and Me_4-cyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) ligands, $[Ge(Me_3\text{-}tacn)]Br[GeBr_3]$ and $[Ge(Me_4\text{-}cyclam)][GeCl_3]_2$ **5** complexes were stabilized. Very recently, Majumdar and coworkers have isolated a germanium dication **6** by taking the advantage of a flexible acyclic tetradentate bis(α-iminopyridine) ligand[9]. Moreover, the formed dication was realized as a ligand for the first time to stabilize metal complexes of Au(I) and Ag(I). In 2015, Braunschweig and coworkers have demonstrated the use of an electron rich coordinatively unsaturated transition metal fragment $[Pt(PCy_3)_2]$ for realizing Sn(II) and Pb(II) dications.[10]

2.2. Objectives

In order to search for new neutral ligands for stabilizing low-valent main group compounds, we have turned our attention to isocyanides, which are stronger σ-donors and weaker π-acceptors than carbon monoxide (Figure 1). Moreover, isocyanides are isoelectronic to NHCs, and therefore the isocyanide metal bond can be described as a carbene-type bond. There are few reports on the reactions of isocyanides with low valent main group compounds such as $[:Ge(ArMe_6)_2]$ [$ArMe_6$ = 2,6-(2,4,6-$(CH_3)_3$–$C_6H_2)_2$–C_6H_3],[11] or the Mg(I) dimer,[12] with regard to the exploration of their reactivity. However, isocyanides have never been examined as ligands for rendering a compound of main group element in low oxidation state. More recently, Braunschweig and coworkers have reported the reactions of terminal borylene complexes with isocyanides to access a base-stabilized boraketenimine and a borylenediisocyanide that displayed the multiple complexations of CO and isocyanides to B; a bonding feature previously not known for main group elements.[13, 14]

Herein, we have introduced the isonitrile as a ligand for stabilizing the Ge(II) dication in a single step.

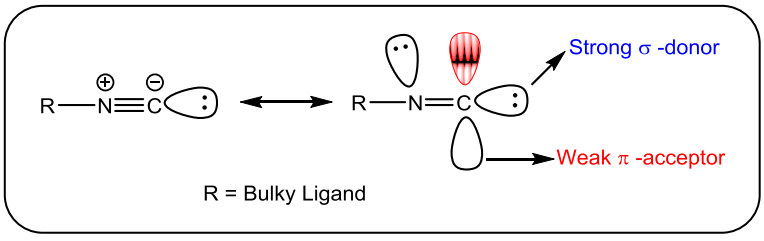


Figure 1. Resonance structures of isocyanide.

The compound was characterized by using state of the art spectroscopic tools as well as single crystal X-ray studies, which shows that four 2,6-dimethylisonitrile molecules are coordinated to the Ge atom having a doubly positive charge in the solid, with two weakly coordinating $GeCl_3$ counter anions.

2.3. Experimental Section

All experiments were carried out under an inert atmosphere of argon applying standard Schlenk techniques or in a glove box. The solvents used were purified by an MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Sigma Aldrich were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded in C_6D_6 and toluene-d_8 using a Bruker Avance DPX 200 or a Bruker Avance DRX 400 spectrometer and were referenced to external $SiMe_4$. However, high-resolution mass spectra (HRMS) were obtained using a Q Exactive Thermo Scientific. Elemental analysis was carried out by CSIR-National Chemical Laboratory, Pune. Melting point was measured in a sealed glass tube on a Stuart SMP-30 melting point apparatus.

2.3.1. Synthesis of 2, 6–dimethylphenylisonitrile 8

2, 6–dimethylaniline (10 g, 82.5 mmol) was dissolved in ethyl formate (15 mL) and then heated under autoclave up to 200 °C overnight. The solid precipitate was filtered off and washed with *n*-pentane. Recrystallization from acetone/petrol ether (1/5) afforded the formamide compound as colorless crystals in almost quantitative yield (11.07 g, 94%). The resultant compound (2.0 g, 13.4 mmol) was dissolved in dry DCM (60 mL). The solution was cooled to –60 °C under inert conditions and phosphorous oxychloride (3.61 mL, 39.02 mmol) was added dropwise over a period of five minutes. The suspension was stirred for the next 20 minutes and triethylamine (16.2 mL, 117 mmol) was added dropwise over a period of 10 minutes at –60 °C. The reaction mixture was changed to an orange color when allowed to warm at room temperature for overnight. Finally, the reaction mixture was poured on to the 50 mL of cold water and washed with DCM (2 x 60 mL). The resultant organic layer was dried with Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was gained as a white crystalline solid compound through sublimation under vacuum ($1.5*10^{-2}$ mbar) at 55 °C (1.54 g, 87.5 %).

^{1}H NMR (200 MHz, C_6D_6, 25 ^{o}C): δ 2.06 (s, 6H, CH_3), 6.60 (d, 2H, 7.68 Hz, Ph), 6.69 (m, 1H, Ph) ppm.

2.3.2. Synthesis of Ge(II) dication 9

A solution of 2, 6–dimethylphenylisocyanide (0.56 g, 4.31 mmol) in toluene (15 mL) was added to $GeCl_2$·dioxane (1.0 g, 4.31 mmol) in toluene (10 mL) at room temperature. The color rapidly changes to brown-red. After stirring the solution overnight, the solvent was removed *in vacuo*. The obtained residue was again extracted with toluene (20 mL) and filtered through celite. The solvent was concentrated (approx. 5 to 7 mL) and cooled to –30 °C for 2 days to give pure Ge(II) dication as yellow crystals suitable for single crystal X-ray analysis.

Yield: 220 mg (5.4%).

^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C): δ 1.92 (s, 24H, CH_3), 6.4 (d, 8H, 8.03 Hz, Ph), 6.65 (m, 4H, Ph) ppm.

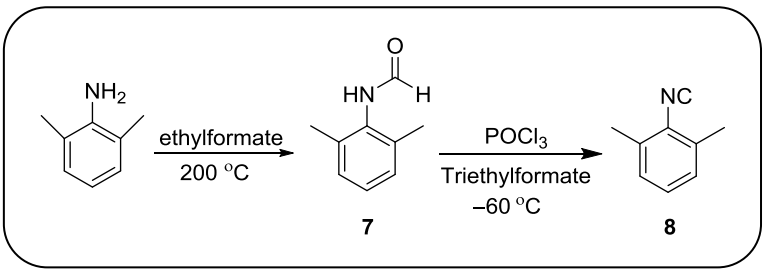
^{13}C NMR (100.6 MHz, C_6D_6, 25 ^{o}C): δ 18.38 (CH_3), 127.18, 130.69, 136.65 (Ph) ppm.
M. P.: 71–73 °C turns dark red color at 75–78 °C.

HRMS *m/z* (%): 955.623 [M^+].

Anal. Calcd for $C_{36}H_{36}Cl_6Ge_3N_4$ (955.9): C, 45.19; H, 3.76; N, 5.85. Found: C, 36.2; H, 3.14; N, 3.74.

2.4. Results and Discussions

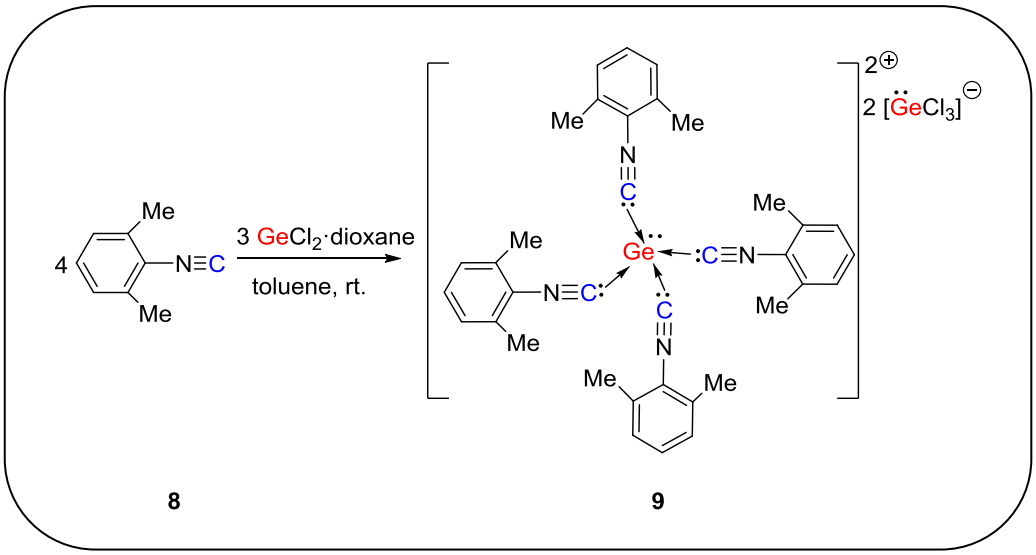
In this work, we have initially prepared the 2,6-dimethylphenylisocyanide **8** from the reaction of *n*-formyl derivative of 2, 6-dimethylaniline **7** (obtained from the corresponding aniline with ethyl formate) with phosphorous oxychloride and triethylamine (addition over a period of 10 min.) in dry DCM (Scheme 1).



Scheme 1. Synthesis of 2,6-dimethylphenylisocyanide **8.**

The Ge(II) dication $[(RNC)_4Ge:]^{2+}[:GeCl_3]_2^-$ **9** was synthesized by addition of one equivalent of 2,6-dimethylphenylisocyanide **8** to a toluene solution of $GeCl_2$·dioxane at ambient temperature. The color of the resultant solution is rapidly changed from colorless to brown-

red (Scheme 2). The Ge(II) dication **9** is soluble in toluene, THF and dichloromethane. The compound is stable at room temperature under an inert atmosphere and characterized by NMR spectroscopic studies.



Scheme 2. Synthesis of Ge(II) dication **9**.

In the ^{1}H NMR spectrum of **9**, a sharp singlet signal at δ 1.92 ppm was observed for the 24 methyl protons, which are slightly shifted upfield in comparison to those of 2,6-dimethylphenylisocyanide (δ 2.06 ppm). Pale yellow crystals of **9** suitable for X-ray diffraction studies were obtained from its saturated toluene solution at −35 °C in a freezer.

The compound was crystallized in the monoclinic space group $P2_1/c$.[15] The asymmetric unit of **9** holds four crystallographically identical isocyanides bound to Ge(II) dication with two weakly coordinating [$GeCl_3$] units (see in Figure 2) as counter anions balancing the charge. The two [$GeCl_3$] ions in the asymmetric unit show no significant bonding interaction with the Ge(II) dication. The closest approach of the chloride atoms of one of the [$GeCl_3$] units is 2.749 Å from methyl hydrogen. The Ge(II) dication is bound to four isocyanide ligands and exhibits a distorted tetrahedral geometry, in which all the bond angles around the Ge atom range from 104.10(15)° to 116.73(16)°. Therefore, the tetrahedral geometry of the Ge(II) atom in **9** is completely different from that in Ge(II) dication **1**, where the Ge(II) center displays pyramidal geometry. Despite the rather bulky nature of the isocyanide ligand, the Ge–C bond lengths in **9** [2.033(4), 2.044(4), 2.044(4), and 2.065(5) Å] fall within the average Ge–C single bond range (1.90–2.05 Å)[17] and are slightly shorter than the Ge–C bond length in the Ge(II) dication **1** (2.070(6) Å)[3] and in [*t*BuNC→{:Ge($ArMe_6$)$_2$}] (2.075(3) Å).[11]

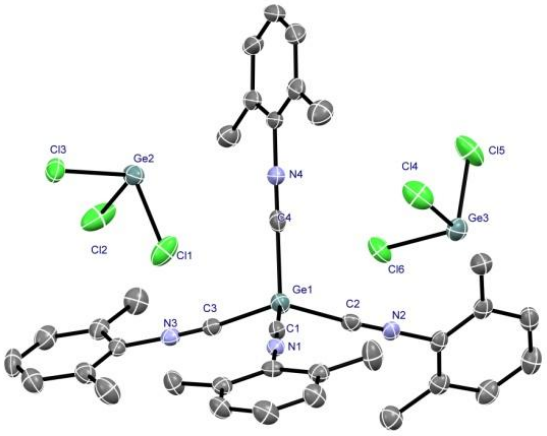


Figure 2. Molecular structure of **9**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (°): Ge1–C1 2.033(4), Ge1–C2 2.044(4), Ge1–C3 2.044(4), Ge1–C4 2.065(5); N1–C1–Ge1 177.3(4), N2–C2–Ge1 176.7(3), N3–C3–Ge1 170.3(3), N4–C4–Ge1 178.1(4), C1–Ge1–C2 111.51(15), C1–Ge1–C3 108.29(15), C2–Ge1–C3 116.73(16), C1–Ge1–C4 112.16(16), C2–Ge1–C4 104.10(15), C3–Ge1–C4 103.78(16), C1–N1–C10 178.5(4), C2–N2–C11 177.4(4), C3–N3–C20 174.9(4), C4–N4–C29 178.2(4).

The four identical isocyanide ligands in compound **9** shows the average N≡C triple-bond lengths are ranging from 1.138(5) Å to 1.142(5) Å and are about the same as in the most free isocyanides (1.14 to 1.16 Å).[18] Three of the four Ge–C–N angles are closer to linearity, ranging from 176.7(3)° to 178.1(4)°, while the residual Ge–C–N angle (170.3(3)°) is slightly bent. The C–N–C bond angle (range 174.9(4)°–178.5(4)°) reveals that the isocyanide ligands are almost linear about the respective nitrogen atoms. It should be mentioned that the non-increase in the C–N bond lengths, and the nearly linear C–N–C angles indicate almost unperturbed isocyanide molecules and annuls the possibility of any back π-bonding from Ge(II) center to C of the isocyanide substituent. In each of the $[GeCl_3]^-$ anions of **9**, three chlorine atoms are covalently bound to the germanium atom, exhibiting a trigonal pyramidal shape of the Ge(IV) center. The average Ge–Cl bond lengths for the anions are 2.277 Å and 2.278 Å, while the average Cl–Ge–Cl bond angles are 96.10° and 95.55°, respectively. These bond lengths and angles are in accordance with the previously reported $[:GeCl_3]^-$ counter anions.[16,18]

2.5. Computational Investigations

We have done the DFT computations of compound **9** to understand the formation and bonding insights. All the calculations were performed at the PBE/TZVP level of theory. We

have initially carried out the geometry optimization of compound **9** for the ground state singlet and triplet geometries.

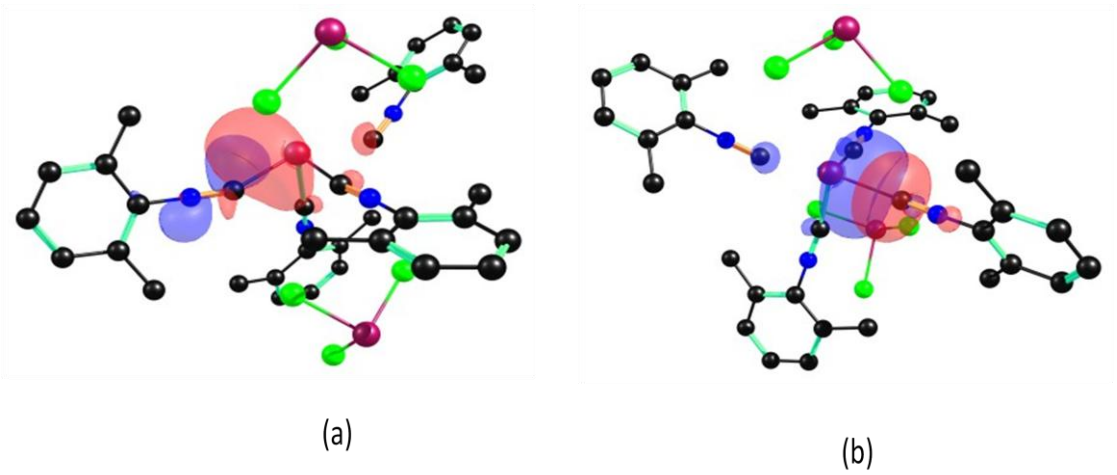


Figure 3. (a) Strong σ (LP (C≡N)→LP(Ge)) interactions and (b) weak π (LP(Ge)→ π^*(C≡N)) interaction

The singlet geometry is considered to be more stable than the triplet by 48.6 kcal mol^{-1}. The optimized geometry of **9** and the corresponding geometrical parameters has been given in Figure 3. As the structure indicates, the central germanium atom is tri-coordinated with three isocyanide ligands, with the two $GeCl_3$ units coming close to the Ge^{2+} center (see in Figure 4).

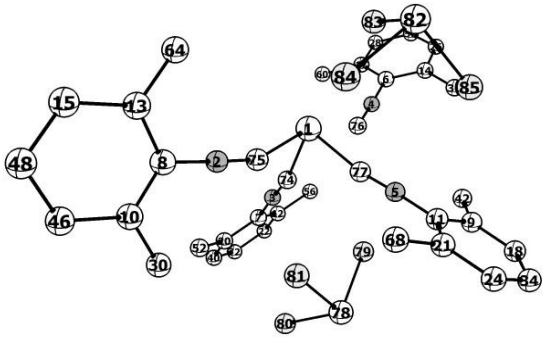
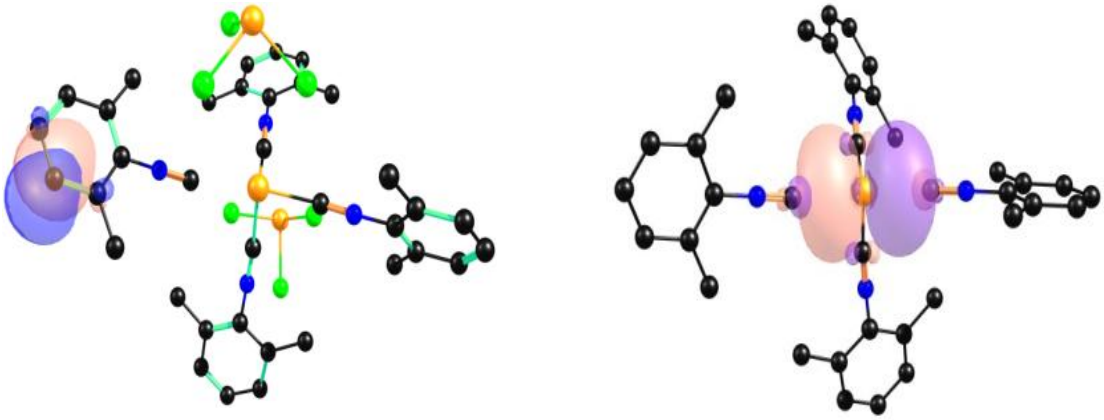


Figure 4. Ge(1)−C(74) = 2.10 Å, Ge(1)−C(75) = 2.22 Å, Ge(1)−C(76) = 2.50 Å, Ge(1)−C(77) = 2.05 Å, C(74)−N(3) = 1.167 Å, C(75)−N(2) = 1.173 Å, C(76)−N(4) = 1.175 Å, C(77)−N(5) = 1.163 Å, Ge(1)−C(74)−N(3) = 164.1°; Ge(1)−C(75)−N(2) = 156.3°; Ge(1) −C(76)−N(4) = 142.0°; Ge(1) −C(77)−N(5) = 170.2°.

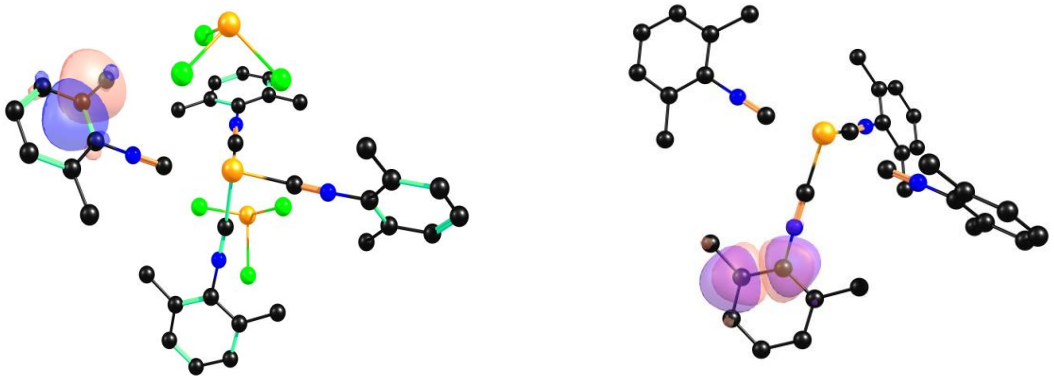
The isocyanide ligands are almost linear about the nitrogen atoms with the C-N-C angles between 176.7° and 177.7°.

This is slightly different from the X-ray structure of **9**, where the four isocyanide ligands were found to be equally coordinated to the central germanium. So as to examine the possibility of displacement of one isocyanide ligand, variable temperature (−70 to 70 °C) ^{1}H NMR spectroscopy analysis of **9** was carried out. However, the VT analysis did not give any evidence of displacement of the isocyanide ligand. The HOMO and LUMO of compound **9** were found to be localized on the phenyl group of the isocyanide ligand that had the weaker coordination to the central germanium (Figure 5(a)).



(a) (b)

Figure 5. (a) HOMO of **9** and (b) HOMO of $\mathbf{9^{2+}}$ (without counter anions) (contour value ±0.03). Hydrogen atoms have been omitted for clarity.



(a) (b)

Figure 6. (a) LUMO of **9** and (b) LUMO of $\mathbf{9^{2+}}$ (without counter anions**)** (contour value ±0.03). Hydrogen atoms have been excluded for clarity.

Also, the structure of the germanium dication (**9**$^{2+}$) without counter anions was optimized in order to determine the nature of the MOs on the dicationic Ge(II) center. It was seen that the HOMO of the germanium dication had the maximum lone pair contribution (Figure 5(b)). This result, in conjunction with the HOMO and LUMO (Figure 6) obtained for **9**, reflects that the nature of the frontier orbitals is appreciably altered when the ion pair complex is considered, rather than just the dication: there is a delocalization away from the Ge^{2+} center when the ion pair is formed. This is likely due to inter-ionic interactions and may be of relevance only for the salt in the solid state, as the ions are likely to be separated to a greater extent in solution. The NBO charge analysis was also done for **9**, and the results indicate that the total positive charge is not localized at the Ge center. The charge on Ge was found to be +0.74 instead of +2 and the RNC groups bonded with the germanium were seen to carry +0.27 charge on average, indicating that the positive charge was delocalized to some extent in the complex.

The bonding in complex **9** was examined by NBO analysis. For compound **9**, it was seen that out of the four RNC groups, two had stronger interactions with the Ge(II) center. For these two, the two most important orbitals correspondes to the relevant σ and π interactions between the central germanium and the isocyanide ligand, with the σ and π energy contributions for the two Ge–C bonds being 118.0 and 48.0, and 21.0 and 2.0 kcal mol^{-1} respectively. Also, the % contributions of the σ interaction for the two Ge–C bonds were seen to be 86% and 96%. Therefore, the data indicates that σ bonding is dominant in the interaction between germanium and the RNC groups.

2.6. Conclusions

One of the remarkable discoveries in Ge(II) cation chemistry is the isolation of a Ge(II) dication by cryptrand.[5] In the succeeding years, the cationic Ge(II) chemistry has undergone a remarkable progress.[6–8] In this chapter, we have introduced isocyanide as a ligand in main group chemistry and showed that 2,6-dimethylphenylisocyanide **8** readily reacts with $GeCl_2$ to afford a Ge(II) dication **9** in a single step. The Ge(II) atom is coordinated to the four isocyanide ligands, has a stereochemically inactive lone pair of electrons and exhibits a distorted tetrahedral geometry. The Ge(II) atoms in the $[:GeCl_3]^-$ moieties adopts a pyramidal geometry. The preparation of the Ge(II) dication by this route will open up a new synthetic strategy for obtaining non-metallic cations and dications.

2.7. References

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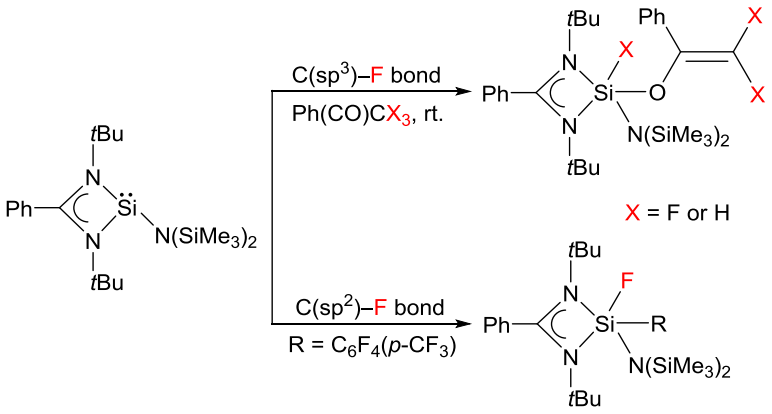
C(sp^3)–F, C(sp^2)–F and C(sp^3)–H Bond Activation at Silicon(II) Center



Abstract

Thermally stable silylene [PhC(N*t*Bu)$_2$SiN(SiMe$_3$)$_2$] **4** activates the C(sp^3)–H and C–F bonds of acetophenone and 1,1,1-trifluoroacetophenone, respectively, at room temperature. DFT calculations revealed that the reaction is initiated *via* a nucleophilic attack from the oxygen to the silicon atom followed by C–F/H bond cleavage. The reactions of silylene **4** with hexafluorobenzene and octafluorotoluene afford the corresponding oxidative products.

3.1. Introduction

The organic compounds with fluorine-comprising groups are crucial in agrochemical, pharmaceutical, and materials science. However, the C–F bond is represents one of the most thermally, photochemically, electrooxidatively and also chemically inert bonds in chemistry, which also renders these molecules extremely long-lived and potentially toxic. The potential application of organofluorine compounds in synthetic organic chemistry and the ever-growing environmental concerns that have become associated with them has encouraged the researchers to develop new synthetic strategies for the activation of C−F bonds. Despite the difficulties associated with C−F bond activation, early and late transition metal-mediated C−F bond transformations have been demonstrated.[1] The realization that compounds with low-valent main group elements can mimic the chemistry of transition metals has led to the burgeoning chemistry of main group compounds centered around their use as reagents for small molecule activation.[2] In recent years examples demonstrating the activation of characteristically strong C–F bonds by N-heterocyclic carbenes (NHCs) have also begun to appear thanks to the extensive works from the groups of Kuhn, Bertrand, Turner, Lee, Baker, Chaplin, Radius, and many others.[3-10] Recently, Studer and co-workers have reported the C–F bond activation in perfluoroarenes by aryl and alkyl isonitriles under UV irradiation.[11] Significant progress has been also made in C–F bond activation by compounds with non-carbon main group elements. In 2017 Mikami et al. have performed the reactions of boryl lithium with fluoroform (CF_3H) and the Ruppert–Prakash reagent (CF_3SiMe_3), gave the corresponding difluoromethyl-substituted derivatives.[12] Using Roesky's NacNac'Al(I) compound, Nikonov and co-workers accomplished the selective oxidative addition of C–F bond of fluoroarenes at room temperature.[13] Recently, Stephan et al. utilized phosphorous Lewis acid such as phosphonium cations (EPCs) for C–F bond activation.[14]

Due to the C−F bond strength (544 kJ/mol) and the resulting high activation energy barrier of the C−F bond, an exceptionally potent Lewis acid with a high fluoride affinity is required. In this regard, the silicon compounds are especially appealing for the C−F bond activation because they can possess both Lewis acidity and fluoride affinity. In 2008 Ozerov et al. reported for the first time the selective aliphatic C−F bond over aromatic C-F bond activation by utilizing a silyliumcarborane catalyst Et_3Si^+ $[CHB_{11}H_5Cl_6]$ in the presence of a silicon(IV) hydride.[15] Later, Müller and co-workers have demonstrated the hydrodefluorination of octafluorotoluene to yield toluene employing a hydride-bridged disilyl cation as the catalyst.[16]

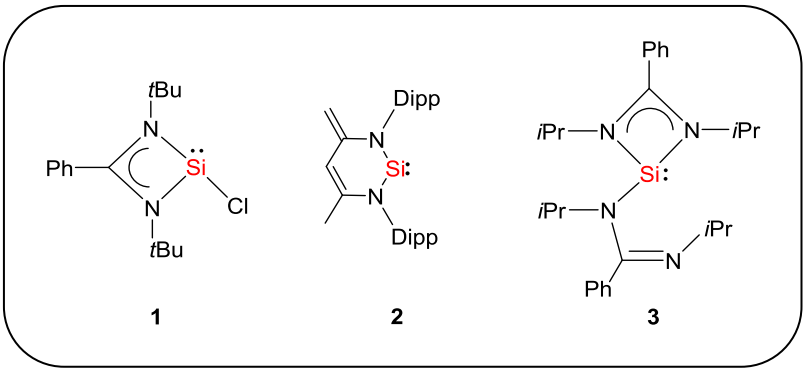


Chart 1. Selected examples of Si(II) centers utilized for C–F bond activations.

More recently, Roesky and coworkers have demonstrated the formal oxidative addition of a C–F bond of hexafluorobenzene, pentafluoropyridine to *N*-heterocyclic silyenes [PhC(N*t*Bu)$_2$SiCl] **1** and [CH{(C=CH$_2$)(CMe)-(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$}Si] **2**.[17,18] Parallel to Roesky's work, Tacke and co-workers reported the activation of hexafluorobenzene with bis-amidinate silylene **3** in toluene at room temperature (Chart 1).[18b] The defluorination of a single C–F bond in trifluoromethyl group is a promising method for preparing difluoro compounds due to the easy availability of trifluoromethylated compounds. However, this remains a formidable synthetic challenge. There are few successful cases of the selective activation of one of C–F bond of trifluoromethylketone. In 1999, Uneyyama et al. have reported the selective defluorination of trifluoromethyl ketones in the presence of Me$_3$SiCl and the reaction was promoted by magnesium.[19]

3.2. Objectives

Neither NHC nor silylene mediated C–F bond activation of a trifluoromethyl ketone has been reported so far. Recently, the reactions of silylene with ketones have been studied by several research groups.[20-22] However, the presence of both the C=O and the C–F bonds in fluoroketones might shed light on how the presence of a neighboring carbonyl unit, itself readily reactive with silylene, would impact C–F bond activation (Figure 1). We have herein accomplished the C–F bond activation of 1,1,1 trifluoro acetophenone by [PhC(N*t*Bu)$_2$SiN(SiMe$_3$)$_2$] **4**,[23] and discussed the reaction mechanism with the aid of DFT computations. Subsequently, we also showed that **4** can activate one of the C(sp^2)−F bonds of hexafluorobenzene and the *para* C–F bond with respect to the CF$_3$ substituent in octafluorotoluene.

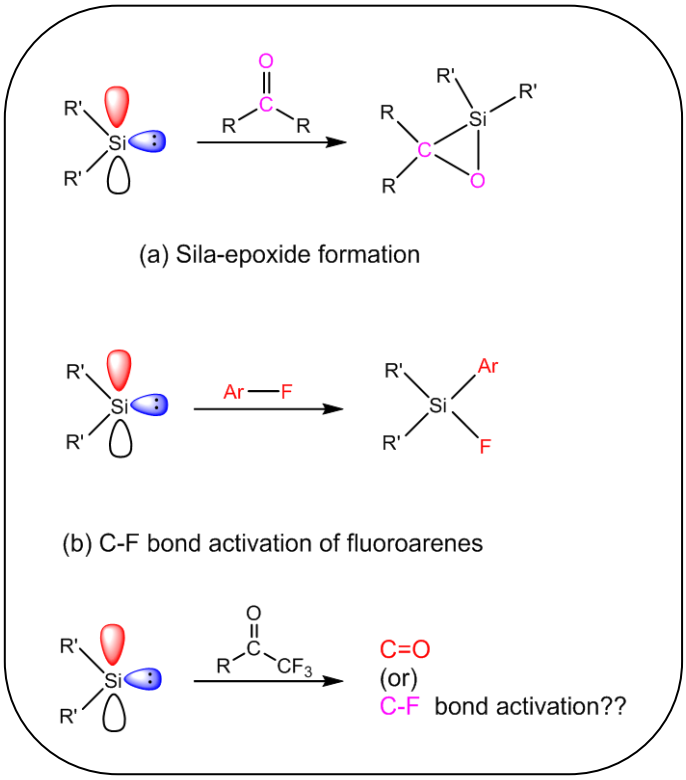


Figure 1. Typical reactions of silylene with (a) carbonyl moieties, (b) perfluoroarenes, (c) the reactions with fluoroketones remain unknown.

3.3. Experimental Section

All manipulations were performed using standard inert atmosphere glove box and Schlenk techniques. Solvents were dried and purified by MBRAUN solvent purification system MB SPS-800. The starting material, [PhC(N*t*Bu)$_2$SiN(Si(CH$_3$)$_3$)$_2$] **4** was prepared according to the literature procedures.[23] acetophenone, hexafluorobenzene, octafluorotoluene and 1,1,1-trifluoromethylacetophenone were purchased from Sigma Aldrich and TCI Chemicals, respectively. They were used without further purification. ^{1}H, ^{13}C, ^{29}Si and ^{19}F NMR spectra were recorded in $CDCl_3$ or C_6D_6 employing a Bruker Avance DPX 200, Bruker Avance DPX 400 or a Bruker Avance DPX 500 spectrometer referenced to external $SiMe_4$, in the case of ^{1}H, ^{13}C and ^{29}Si NMR and $CFCl_3$ for the ^{19}F NMR spectra, respectively. Elemental analysis was performed by CSIR-National Chemical Laboratory, Pune. Furthermore, Melting points were measured in a sealed glass tube on a Stuart SMP-30 melting point apparatus.

3.3.1. Preparation of [PhC(N*t*Bu)$_2$]SiFN(Si(CH$_3$)$_3$)$_2$ (OC(Ph)=CF$_2$) 5

The toluene solution (10 mL) of trifluoromethylacetophenone (0.083 g, 0.47 mmol) was added drop by drop to the toluene solution (10 mL) of silylene **4** (0.2 g, 0.47 mmol) at ambient conditions. After 6h ^{19}F NMR spectrum recorded and indicated the formation of

product. The solution was removed under reduced pressure and extracted with hexane (15 mL). The hexane solution was then concentrated (5 mL) and placed at room temperature for one day, affording colorless, X-ray quality crystals of **5** in 92.1% yield.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 0.10 (s, 18H, $(SiMe_3)_2$), 0.94 (s, 18H, *t*Bu), 7.14-7.38 (m, 10H, Ph) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 1.19 ($SiMe_3$), 5.64 ($SiMe_3$), 31.54 (*t*Bu), 54.27 (*t*Bu), 134.34 (CF_2), 114.69, 114.87, 115.05, 115.25, 127.68, 127.68, 128.09, 128.58, 129.90, 133.68, 151.25, 154.03 (Ph), 156.86 (C(O)Ph), 172.79 (NCN) ppm.

^{19}F NMR (376.63 MHz, $CDCl_3$, 25 °C): δ −93.76 (s, 1F, Si−F), −102.32 (d, , J = 75.32, 1F, CF_2),−117.76 (d, J = 75.32 Hz, 1F, CF_2) ppm.

^{29}Si{^{1}H}NMR (79.53 MHz, $CDCl_3$, 25 °C): δ 3.80 ($SiN(SiMe_3)_2$), −107.06 (d, J = 236.71Hz, Si−F) ppm.

M. P.: 128.9 °C.

Anal. Cacld for $C_{29}H_{46}F_3N_3OSi_3$: C, 58.64; H, 7.81; N, 7.07. Found: C, 56.83; H, 7.05; N, 6.90.

3.3.2. Preparation of $[PhC(N\textit{t}Bu)_2]SiHN(Si(CH_3)_3)_2$ $(OC(Ph)=CH_2)$ 6

The toluene solution (10 mL) of acetophenone (0.057 g, 0.47 mmol) was added drop by drop to the toluene solution (10 mL) of silylene **4** (0.2 g, 0.47 mmol) at room temperature. After 6h ^{1}H NMR spectrum recorded and indicated the formation of product. The solution was completely removed under reduced pressure, affording the colorless oily liquid. The formed compound was submitted for spectroscopic studies which were supported the pure product formation of **6**.

Yield: 0.226 g (87.8%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 0.19 (s, 18H, $(SiMe_3)_2$), 1.13 (s, 18H, *t*Bu), 4.44 (br, 1H, C ═ CH_2), 4.75 (br, 1H, C ═ CH_2), 5.17 (s, 1H, Si–H), 7.17-7.64 (m, 10H, Ph) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 5.08 ($SiN(SiMe_3)_2$), 32.02 (*t*Bu), 54.59 (*t*Bu), 88.95 (C ═ CH_2), 126.14, 127.59, 127.80, 128.32, 129.28, 129.44, 137.03, 139.87 (Ph), 157.44 (C(O)Ph), 166.63 (NCN) ppm.

^{13}C-DEPT NMR (100.6 MHz, $CDCl_3$, 25 °C); δ 4.73 ($SiN(SiMe_3)_2$), 31.82 (*t*Bu), −88.60 (C ═ CH_2), 125.79, 127.43, 127.53, 127.65, 127.71, 128.16, 129.12, 129.28 (Ph), ppm.

^{29}Si{^{1}H}NMR (79.53 MHz, $CDCl_3$, 25 °C): δ 2.59 ($N(SiMe_3)_2$), −81.12 (Si – H) ppm.

Anal. Cacld for $C_{29}H_{49}N_3OSi_3$: C, 64.51; H, 9.15; N, 7.78. Found: C, 62.96; H, 8.47; N, 5.89.

3.3.3. Preparation of $[PhC(NtBu)_2]SiFN(Si(CH_3)_3)_2$ (C_6F_5) 7

The toluene solution (10 mL) of hexafluorobenzene (0.097 g, 0.52 mmol) was added drop by drop to the toluene solution (10 mL) of silylene **4** (0.2 g, 0.47 mmol) at room temperature. The resulting reaction mixture was stirred overnight and placed in a hot oil bath at 70−90 ^{o}C. The solution was removed under reduced pressure and extracted with toluene (15 mL).The solvent was concentrated to about 5mL and placed in a refrigerator at –30 ^{o}C for five days, giving a colorless, X-ray quality crystals of **7** in 85.4% yield.

^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C): δ 0.25 (s, 18H, ($N(SiMe_3)_2$), 0.86 (s, 9H, *t*Bu), 1.12 (s, 9H, *t*Bu), 7.24-7.30 (m, 5H, Ph) ppm.

^{13}C NMR (100.6 MHz, C_6D_6, 25 ^{o}C): δ 5.38 ($N(SiMe_3)_2$), 32.29, 32.32 (*t*Bu), 52.48, 55.46 (*t*Bu), 127.31, 127.95, 128.47, 129.35, 133.43, 136.23, 140.93, 153.04 (Ph), 166.45 (NCN) ppm.

^{19}F NMR (376.63 MHz, C_6D_6, 25 ^{o}C): δ −89.09 (s, 1F, Si−F), −125.53 (br, 2F, *o*-F), −154.97 (t, $^3J(^{19}F–^{19}F$ = 22.59 Hz, 1F, *p*-F)), −162.19 (br, 2F, *m*-F) ppm.

^{29}Si{^{1}H}NMR (79.53 MHz, C_6D_6, 25 ^{o}C): δ −16.77 ($SiN(SiMe_3)_2$), −62.17 (d, J = 243.19 Hz, Si −F) ppm.

M. P.: 148.3 °C.

Anal. Cacld for C_{27} H_{41} F_6 N_3 Si_3: C, 53.52; H, 6.82; N, 6.94. Found: C, 51.32; H, 6.67; N, 6.22.

3.3.4. Preparation of $[PhC(NtBu)_2]SiFN(Si(CH_3)_3)_2$ (4-$C_6F_4CF_3$) 8

The toluene solution (8 mL) of octafluorotoluene (0.112 g, 0.47 mmol) was added drop by drop to the toluene solution (10 mL) of silylene **4** (0.2 g, 0.47 mmol) at ambient conditions. The reaction mixture was stirred overnight and transformed to a pale yellow color. The solvent was completely removed under reduced pressure and extracted with toluene (15 mL). The final compound was passed through celite, solvent was removed under vacuum and the

following filtrate was reduced to 4 to 6 mL. Good quality of colorless crystal **8** was gowned when crystallization was performed in toluene at –30 °C in a freezer.
Yield: 0.248 g (79.3%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ 0.36 (s, 18H, ($N(SiMe_3)_2$), 0.95 (s, 18H, *t*Bu), 7.26-7.36 (m, 5H, Ph) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^{o}C): δ 1.2 ($SiMe_3$), 5.16 ($SiMe_3$), 32.21 (*t*Bu), 55.45 (*t*Bu), 127.40, 127.80, 127.92, 128.33, 129.55, 135.35 (Ph), 167.63 (NCN) ppm.

^{19}F NMR (376.63 MHz, $CDCl_3$, 25 ^{o}C): δ −56.25 (t, 4*J* (19F−19F = 22.59 Hz, 3F, CF_3), −85.09 (s, 1F, Si−F), −124.04 (br, 2F, *o*-F), −141.37 (br, 2F, *m*-F) ppm.

^{29}Si{^{1}H}NMR (79.53 MHz, $CDCl_3$, 25 ^{o}C): δ − 20.02 ($SiN(SiMe_3)_2$), − 71.28 (d, *J* = 245.02Hz, Si −F) ppm.

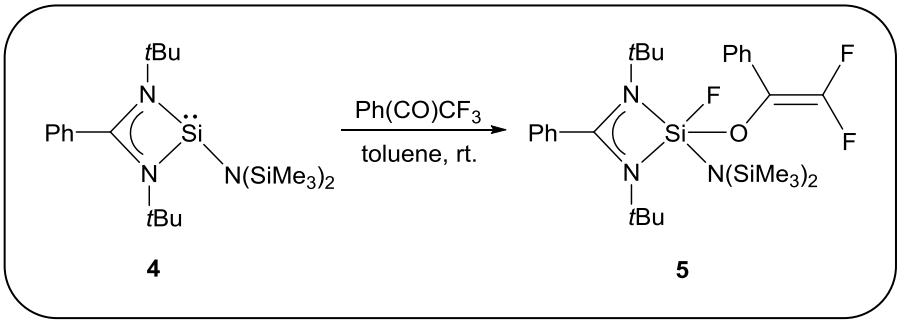
M. P.: 97.4 °C.

Anal. Cacld for $C_{28}H_{41}F_8N_3Si_3$: C, 51.27; H, 6.30; N, 6.41. Found: C, 49.69; H, 6.13; N, 5.87.

3.4. Results and Discussions

3.4.1. Synthesis and characterization of compound 5

The readily available silylene **4** was selected as a starting material for the C–F bond activation of fluoroketone. When the compound **4** was reacted with 1,1,1 trifluoro acetophenone at ambient conditions, it did not afford either the sila-epoxide formation or simple C–F bond activation but a difluorinated alkene **5** containing both Si–O and Si–F bond (Scheme 1).



Scheme 1. Activation of C–F bond of trifluoro acetophenone by **4** and the formation of **5**.

In ^{19}F NMR spectroscopy, the fluorine signals are appeared at δ −93.76 (s, 1F, Si−F), −102.21,−102.41 (d, J_{F-F} = 75.32 Hz, 1F, CF_2),−117.68, −117.88 (d, J_{F-F} = 75.32 Hz, 1F, CF_2)

ppm, indicating that the selective activation of one of the C–F bonds of trifluoromethylacetophenone by **4.** The ^{29}Si NMR resonance is observed at δ –107.06 ppm ($J_{Si–F}$ = 236.71 Hz) as a doublet reflecting the formation of a penta-coordinate silicon compound. The ^{13}C NMR spectrum shows two new alkene carbon peaks at δ 156.86 and 134.34 ppm due to the formation of a double bond between C_{22} and C_{23}.

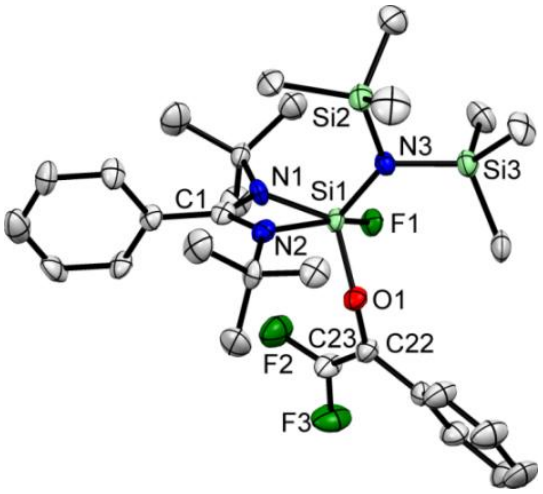


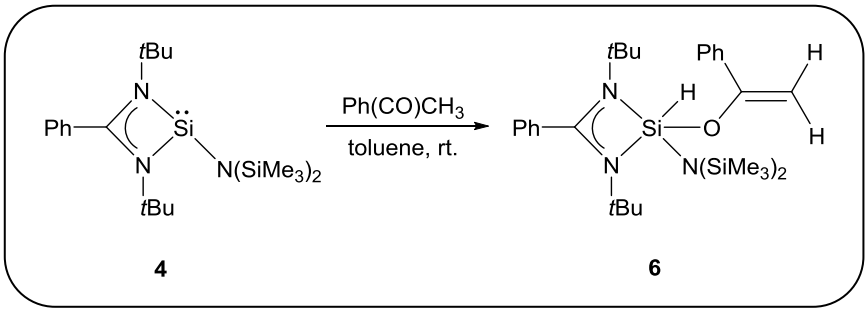
Figure 2. Molecular structure of **5**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°): Si1–F1 1.649(5), Si1–O1 1.694(4), Si1–N3 1.732(7), Si1–N1 1.813(7), Si1–N2 1.965(7), C22–C23 1.30(1), C23–F2 1.32(1), C23–F3 1.32(1); F1–Si1–O1 92.0(3), F1–Si1–N3 99.0 (3), O1–Si1–N3 114.5(3), F1–Si1–N1 93.3(3), O1–Si1–N1 125.6(3), N3–Si1–N1 118.0(3), F1–Si1–N2 156.2(3), O1–Si1–N2 86.9(3), N3–Si1–N2 103.1(3), N1–Si1–N2 68.6(3), N3–Si1–N1 118.0 (3), C1–N1–Si1 94.2(5), C1–N2–Si1 88.8(5).

The compound **5** was isolated as colorless crystalline solid with good solubility in solvents such as benzene and toluene. Furthermore, it was stable in solution or in the solid state at room temperature in an inert atmosphere. The molecular structure of **5** was confirmed by crystal structure analysis (Figure 2). Compound **5** crystallizes in the orthorhombic space group $P2_12_12_1$. The amidinate ligand is coordinated in a *N*,*N*'-chelate fashion to the silicon(IV) center and one nitrogen from the amide substituent moiety, one oxygen, and one fluorine atom from trifluoromethylacetophenone moiety and displays a distorted trigonal bipyramidal geometry. The Si1–F1 bond length (1.649(5) Å) in **5** is comparable to that in in $PhC(NtBu)_2SiF_3$ (1.5988(6) Å and 1.5947(7) Å).[24] The bond length of $Si–N_{amidinate}$ is 1.732(7) Å, which is significantly shorter than the $Si–N_{amidinate}$ bond lengths (1.812(7) and 1.965(7) Å).

The Si–O bond length in **5** (1.694(4) Å) is in the normal range for a Si–O single bond.[25] The bond distance between C_{22} and C_{23} (1.30(1) Å) due to the formation of double bond.

3.4.2. Synthesis and characterization of compound 6

The reaction of acetophenone with one equivalent of **4** in toluene at room temperature afforded a colorless solution (Scheme 2). Upon removal of solvent the compound **6** was formed as a white color precipitate in 87.8% yield and confirmed by NMR spectroscopic studies. The ^{1}H NMR spectrum of **6** exhibits one resonance at δ 5.17 ppm, which indicates the silicon hydride bond formation. Moreover, it shows two broad signals at δ 4.44 and 4.75 ppm that result from the C=CH_2 unit. The ^{13}C and DEPT-135 NMRs displayed the single resonances for the terminal alkene (CH_2) at 88.95 ppm and –88.60 ppm, respectively. The appearance of only singlet signal for the trimethylsilyl groups in ^{1}H (δ 0.19 ppm) as well as ^{29}Si NMR (2.59 ppm) indicates that they are chemically equivalent. The ^{29}Si NMR spectrum showed a resonance at δ −81.12 ppm and this could be assigned to the penta-coordinate Si atom in **6** which is more downfield shifted than in **5**.

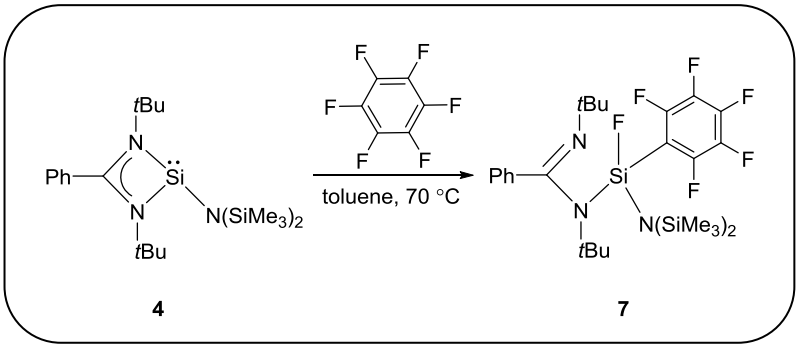


Scheme 2. C–F bond activation of acetophenone by **4** and formation of **6**.

3.4.3. Synthesis and characterization of compound 7

In addition to this, the scope of C–F bond activation was further explored with hexafluorobenzene and octafluorotoluene. Both of these fluorinated molecules were known to undergo aromatic C–F bond activation with silylenes. However, the reaction of hexafluorobenzene with [PhC(N*t*Bu)$_2$SiCl] in toluene-d_8 at 120–130 °C for 24 h, afforded the oxidative C–F bond product of [PhC(N*t*Bu)$_2$SiCl], but the X-ray structure was not reported.[17] **4** is a less reactive silylene due to the protection of the lone pair of electron on silicon by two bulky trimethylsilyl ligands. Gratifyingly, **4** react with hexafluorobenzene at 70 °C and activates one of the C–F bonds leading to the formation of **7** in good yield (Scheme 3). The formation of **7** was confirmed by ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectroscopic studies. In the ^{19}F NMR spectrum of **7**, the resonances were appeared at δ −89.09 (s, 1F, Si–

F),−125.53 (br, 2F, *o*-F), −154.97 (t, $^{3}J(^{19}F–^{19}F$ = 22.59 Hz, 1F, *p*-F)), −162.19 (br, 2F, *m*-F) ppm, indicates the activation of one of C–F bond of hexafluorobenzene. The appearance of the ^{29}Si NMR signal at δ −62.17 ppm for **7** shows the formation of four coordinate silicon in solution.



Scheme 3. C–F bond activation of hexafluorobenzene by **4** and formation of **7**.

The compound **7** was obtained as a colorless crystalline solid and stable under an inert atmosphere. Compound **7** crystallized in the monoclinic space group $P2_1/C$, is shown in Figure 3. However, one of the Si–N bonds from the amidinate ligand moiety was seen to be opened.[26] Evidence for this behaviour comes from the Si(1)–N(2) interatomic separation (2.565 Å), which conclusively suggests that there is not even a weak interaction between Si1 and N2. This observation was further confirmed by the differing C–N bond lengths [C1–N1 1.389(4) Å *vs*. C1–N2 1.289(3) Å] in the benz-amidinato fragments. The central silicon atom in compound **7** is four-coordinate and exhibits a distorted tetrahedral geometry. The Si1–F1 bond length is 1.618(2) Å, which is significantly shorter than that of Si–F bond of **5** (1.649(5) Å). Moreover, the Si1–C22 (1.895(4) Å) bond is in the normal range of their single bond.

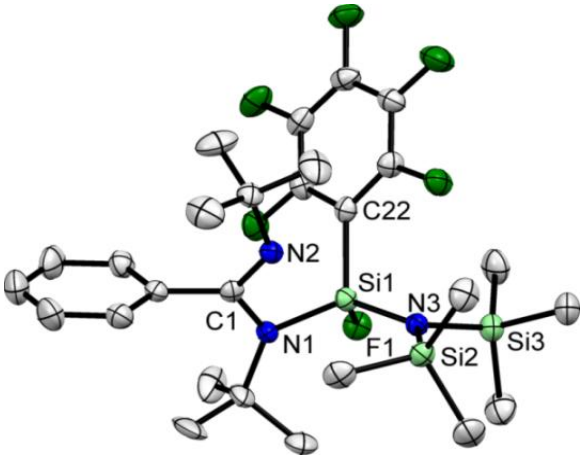
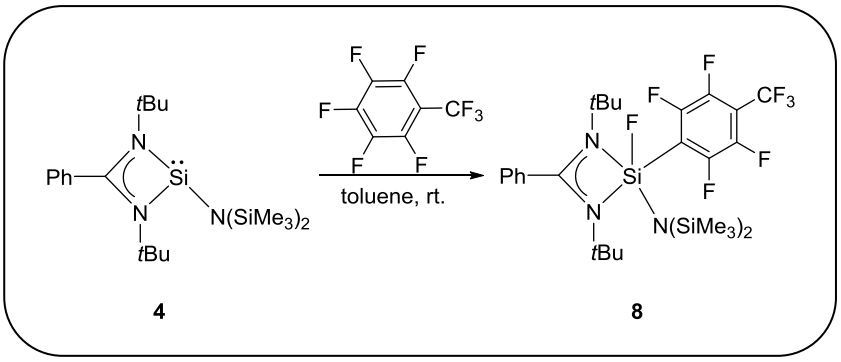


Figure 3. Molecular structure of **7**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å)

and angles (°): Si1–F1 1.618 (2), Si1–N3 1.703(3), Si1–N1 1.740(3), Si1–C22 1.895(4), C1–N1 1.389(4), C1–N2 1.289(3); F1–Si1–N3 103.2(1), F1–Si1–N1 100.8(1), N3–Si1–N1 121.5 (1), F1–Si1–C22 96.6(1), N3–Si1–C22 114.0(1), N1–Si1–C22 115.00(1).

3.4.4. Synthesis and characterization of compound 8

The treatment of octafluorotoluene with one equivalent of **4** in toluene for 12 h at room temperature, regiospecifically afforded the silicon(IV) fluoride derivative **8**, with no evidence of the more inert C(sp^3)−F bond activation (Scheme 4). The regioselectivity was observed due to the decreased bond strength of the C(sp^2)–F bond, in comparison to the C(sp^3)–F bond. Upon increasing the number of fluorine atoms in perfluorinated arenes, the C–F bond strength decreases. As a result, the C–F bond activation barrier also decreases. This is apparent in the aforementioned reactions, as the activation of hexafluorobenzene takes place at 70 °C, while the activation of octafluorotoluene takes place at room temperature.



Scheme 4. Activation of octafluorotoluene by **4** and formation of **8**.

Moreover, we also found that there was no cleavage of the Si–$N_{amidinate}$ bonds in compound **8**.[27] In the solid-state structure of **8**, the central Si atom features an approximately trigonal bipyramidal geometry, with C22, N2 and N3 occupying equatorial positions while F1 and N1 filled the axial positions, which is in accordance with the VSEPR model (Figure 4). The Si–F (1.640(3) Å) and Si–C (1.936(5) Å) bond lengths are only marginally longer than their respective equivalent bonds in **7**. Both **7** and **8** may be considered as the products of an oxidative addition of the C(sp^2)−F bond of perfluoroarenes to silylene. In the ^{19}F NMR spectra of compounds **7** and **8**, the Si-F resonances detected at δ –89.09 and –85.09 ppm, respectively. The ^{29}Si NMR spectrum shows doublets at δ −62.17 ppm for **7** and −71.28 ppm for **8** with a coupling constant of ^2J(^{29}Si-^{19}F) 243.19 and 245.02 Hz, respectively.

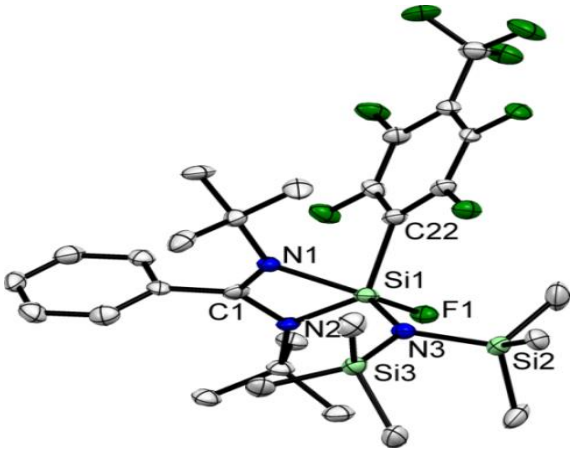


Figure 4. Molecular structure of **8**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°):Si1–F1 1.640(3), Si1–N3 1.715(4), Si1–N2 1.793(4), Si–N1 2.069(4), Si1–C22 1.936(5); F1–Si1–N3 99.2 (2), F1–Si1–N2 94.2 (2), N3–Si1–N2 119.5(2), F1–Si1–C22 89.0 (2), N3–Si1–C22 118.9(2), N2–Si1–C22 120.1(2), F1–Si1–N1 155.5(2), N3–Si1–N1 103.8(2), N2–Si1–N1 67.3(2), C22–Si1–N1 87.1(2), C1–N2–Si1 98.1(3), C1–N1–Si1 86.9(3).

3.5. Computational Investigations

Full quantum chemical calculations have been carried out with density functional theory (DFT) using the PBE/TZVP level of theory. In order to gain more insight into the reaction mechanism (see in Figure 5) of C-F bond activation of 1,1,1-trifluoromethylacetophenone by **4**. The reaction mechanism first proceeds through the transition state **TS_1**, with an corresponding energy barrier (ΔG) of 67.8 kJ/mol, in which the Si-O bond is formed and the C-O bond is changed from a double bond to a single bond, leading to the intermediate **Int_1**. Then, the reaction continues through a five membered transition state **TS_2**, with the corresponding energy barrier of 6.8 kcal/mol, where a Si-F bond and a C-C double bond are formed. The final product **Pdt** is thermodynamically very much stable (-174.5 kJ/mol), which, along with the low barriers obtained, suggests that this reaction is both kinetically and thermodynamically feasible at ambient conditions.

The replacement of C–F bond with C–H bond is result in electron density shift towards the carbon terminus.[28] Therefore, the next compelling question is whether **4** can activate the C–H bond of CH_3 functionality or undergo Murai type reactions[29] or form the typical [1+2] cycloaddition product with acetophenone.[21, 22] Silylene mediated C–H activation has been reported but the majority of the reactions target an aromatic C–H bond.[30] Along the

same lines, the C–H activation of acetophenone with many late transition metal catalysts is known but in all cases, it was the aromatic C-H bond that was seen to be activated resulting in the orthometallated product, while the CH_3 functionality was left intact.[31]

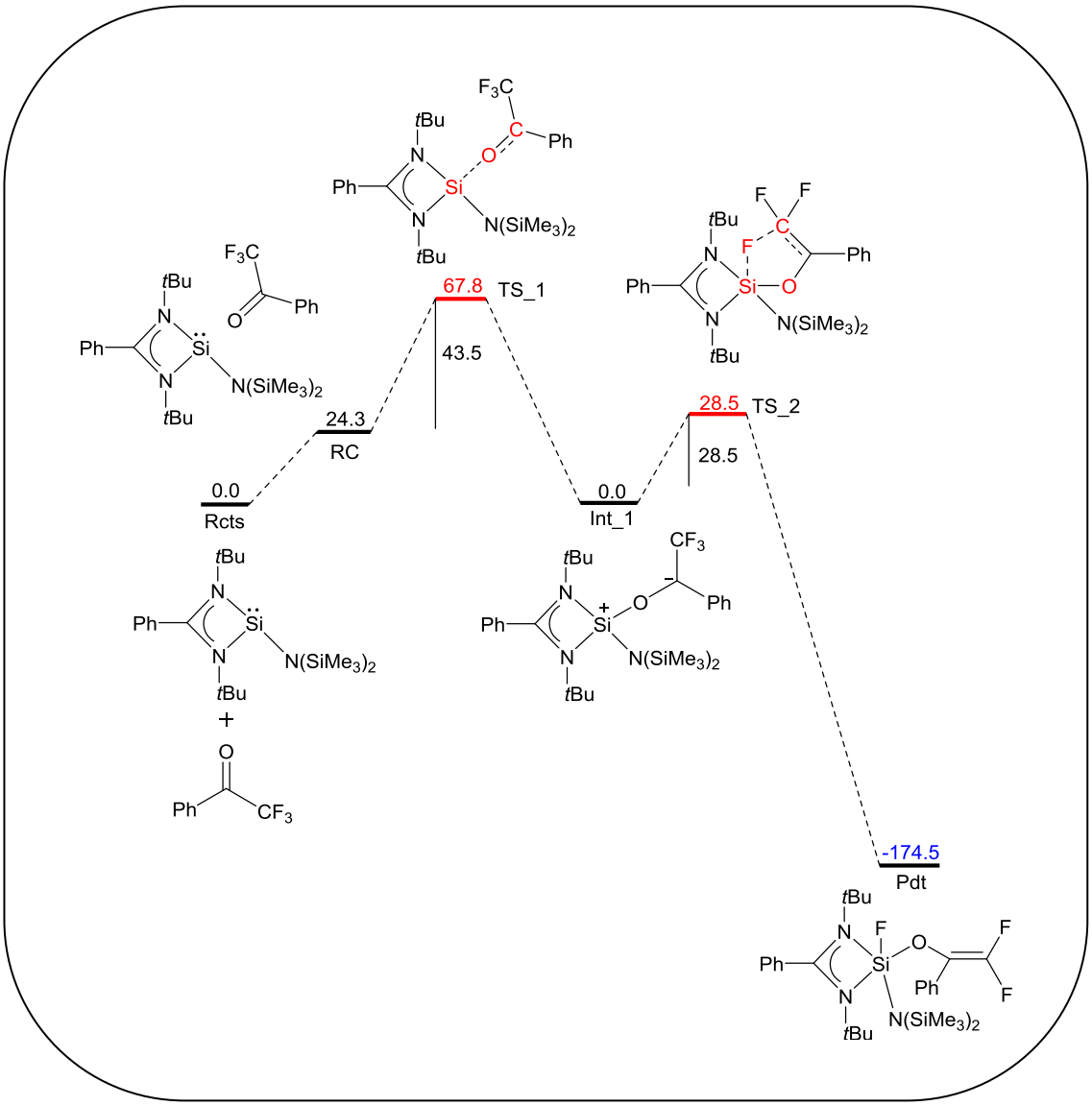


Figure 5. The reaction energy profile diagram for the C–F bond activation of fluoroketone by **4**. The values (in kJ/mol) have been calculated with DFT at the PBE/TZVP level of theory.

3.6. Conclusions

We have demonstrated in this chapter the activation of one of the C(sp^3)–F bonds of trifluoroacetophenone by silylene at room temperature. The analogous reaction with acetophenone led to selective C(sp^3)–H activation instead of C(sp^2)–H bond activation. The DFT computations were carried out to understand the reaction mechanism of fluorinated ketone with **4**. Moreover, the oxidative addition of one of the C–F bonds of

hexafluorobenzene as well as the *para* C–F bond of octafluorotoluene relative to the CF_3 moiety to a Si(II) center has also been examined. These results demonstrated the fact that the tendency of silylenes to undergo oxidative addition can be exploited to activate such inert bonds.

3.7. References

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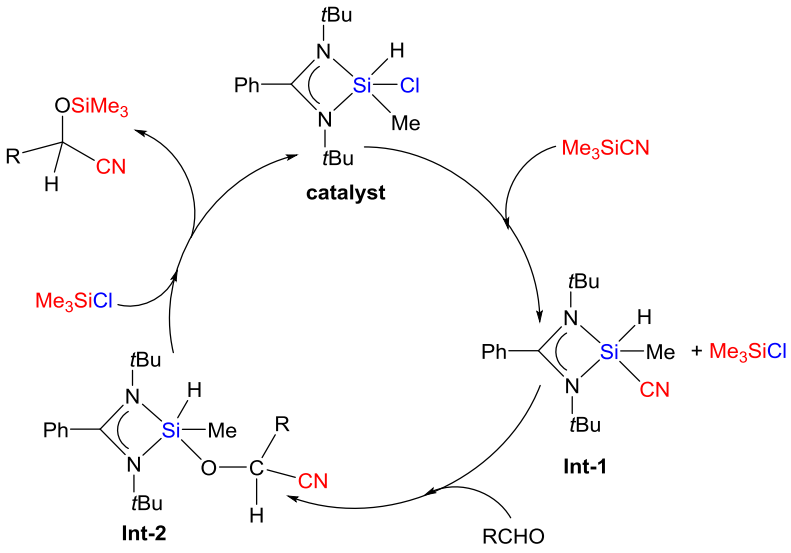
Selective Aldehyde Cyanosilylation by a Neutral Penta-Coordinate Silicon Compound



Abstract

The present study is focused to the synthesis and characterization of a neutral penta-coordinate Si(IV) hydride ($PhC(NtBu)_2SiH(CH_3)Cl$) **5**. We have used it as a catalyst for the reaction of aldehydes with trimethylsilylcyanide (TMSCN) at room temperature. Compound **5** represents the first neutral penta-coordinate silicon(IV) species that catalyzes cyanosilylation of aldehydes under mild conditions. Aliphatic, aromatic and heterocyclic aldehydes can be converted to the corresponding cyanosilylated products in high yields. In this work, we have proposed a highly favorable reaction mechanism based on NMR experiments that led to the isolation of one of the key intermediate, **6**.

4.1. Introduction

The utilization of compounds with heavier *p*-block elements in usual oxidation state as single site catalysts is a thriving field of metal free hydroboration.[1-12] There has been a keen interest among the metal free catalyzed reactions, in which the cyanosilylation of aldehydes is the most important strategies due to the formation of C–C bond and the protection of alcohol functionality. The functionaliztion of these resultant compounds like cyanohyrdins is of current interest and results in the formation of α-hydroxy carbonyl, α-amino acids, and β-amino alcohol derivatives, which have versatile importance in agrochemical as well as in pharmaceutical industry. There has been an increased interest in nonmetallic catalytic systems for cyanosilylation of aldehydes with TMSCN because of the toxicity and difficulty in handling HCN, another reagent for transfering CN group to carbonyl substrates.[13] However, the studies of a well-defined heavier main group compounds as a metal free single site cyanosilylation catalysts are very limited (Chart 1). In 2014, Nagendran et al. reported a Ge(II) cyanide **1** as a catalyst for the cyanosilylation of three aldehydes at room temperature.[14] Bergman and Tilley have only catalyzed the silacyanation of 4-nitro-benzaldehyde using bis(perfluorocatecholato)silane [$Si(cat^F)_2$] **2** catalyst.[15] More recently, the research groups of Zhi, Parameswaran, and Roesky utilized a well-defined Al(III) hydride catalyst [(LAlH(OTf)) (L = $HC(CMeNAr)_2$, Ar = 2,6-*i*$Pr_2C_6H_3$)] **3** for the silacyanation of a range of aldehydes and ketones.[1, 16]

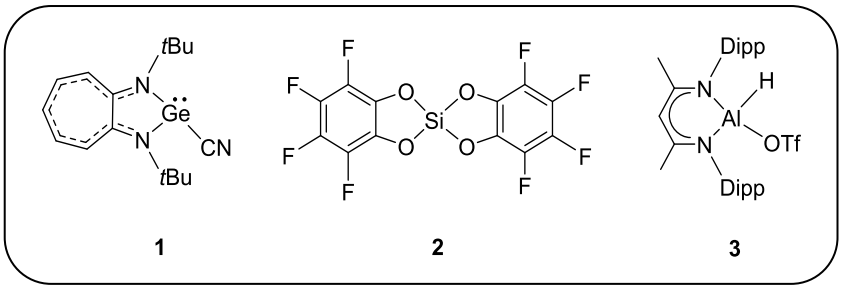


Chart 1. Previously reported heavier main group *p*-block catalysts for cyanosilylation of carbonyl compounds.

Catalysis with silicon compounds amongst the heavier *p*-block elements seems to offer many advantages because silicon is the (a) isostere of carbon, (b) non-metal, (c) silicon precursors are cheap and less toxic, and (d) the second most earth abundant element. In spite of these priori favorable attributes as well as impetus from the theoretical studies,[16] neutral well-defined silicon Lewis acids are relatively rare[5,17,18] and largely restricted to silylium ions. [19]

4.2. Objectives

The cyanosilylation of aldehydes with trimethylsilylcyanide using non-metallic catalyst systems are of current interest. This is attributed to the formed cyanohydrins which are extremely versatile synthetic precursors, can be freely transformed into α-hydroxy carbonyl derivatives, α-amino acids, and β-amino alcohols for their utilization in agrochemicals and pharmaceuticals. Herein, we have reported the synthesis of a Si(IV) hydride ($PhC(N\textit{t}Bu)_2SiH(CH_3)Cl$), **5** employing amidinato ligand and explored as a potential catalyst for cyanosilylation of a variety of aromatic and aliphatic aldehydes with trimethylsilylcyanide under mild reaction conditions. To the best of our knowledge, this is the first example of a neutral penta-coordinate Si(IV) compound that catalyzes aldehyde cyanosilylation at room temperature.

4.3. Experimental Section

All synthesis and catalytic experiments were carried out using standard Schlenk and glove box techniques under a purified argon atmosphere. Toluene, *n*-hexane, CH_2Cl_2, and THF were dried and purified by an MBRAUN solvent purification system MB SPS-800. Benzene was dried and distilled using Na/benzophenone mixture for performing all the catalytic reactions. *N*,*N*'-Ditertiarybutylcarbodiimide and phenyl lithium were purchased from Sigma Aldrich and used without further purification. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker Avance DPX 200 or Bruker Avance DPX 500 spectrometer referenced to external $SiMe_4$. High resolution mass spectra were obtained using a Q Exactive Thermo Scientific. The microanalyses and FTIR experiments were carried out. Furthermore, Melting points were measured in a sealed glass tube on a Stuart SMP-30 melting point apparatus.

4.3.1. Synthesis of compound 5

The solution of *N*,*N*'-Ditertiarybutylcarbodiimide **4** (2.0 g, 12.9 mmol) in toluene (80 mL) was cooled to –78 ℃ and PhLi (6.78 mL, 12.9 mmol 1.9 M in diethylether) was added dropwise over 10 minutes. The resulting suspension was slowly warm to room temperature and stirred for 4h. The solution was again cooled to –78 ℃ and dichloromethylsilane was added over 5 minutes, *via* cannula. The final mixture was then allowed to room temperature and stirred for further 16 h, affording a pale yellow color solution. The resultant mixture was formed the white precipitated, which indicates the formation of lithium chloride during the reaction. Volatiles were removed in a *vacuo* and the residue extracted with toluene (50 mL). The extract was filtered and the filtrate was concentrated to 10 to 15 mL. This afforded a

highly crystalline product within a day when crystallization was carried out in toluene at –30 °C in a freezer.

Yield: 3.786 g (94.6%).

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ 0.87 (s, 3H, CH_3), 1.13 (s, 18H, *t*Bu), 5.98 (s, 1H, Si-H), 7.31-7.47 (m, 5H, Ph) ppm.

^{13}C NMR (125.72 MHz, $CDCl_3$, 25 ^{o}C): δ 8.62 ($SiCH_3$), 32.06 (CMe_3), 55.10 (CMe_3), 127.94, 128.66, 130.29, 133.29 (Ph), 172.06 (NCN) ppm.

^{29}Si{^{1}H}NMR (99.36 MHz, $CDCl_3$, 25 °C): δ -88.60 ppm.

M. P.:108.6 °C.
IR (KBr, cm^{-1}): υ 2160.70.

Anal. Cacld for $C_{16}H_{27}N_2ClSi$: C, 61.80; H, 8.75; N, 9.01. Found: C, 58.94; H, 8.43; N, 8.01. HRMS (ESI, *m/z*): calcd: 310.16, found: 310.23 $[M]^+$, 309.23 $[M-H]^+$.

4.3.2. Synthesis of compound 6

The solution of compound **5** (0.31g, 1mmol) in 20 mL of toluene was added dropwise to the solution of trimethylsilylcyanide (0.0992g, 1mmol) in toluene (10 mL) at room temperature. The resulting suspension was stirred further for 3 h. Volatiles were removed in a *vacuo* and extracted with toluene (20 mL). The final mixture was filtered through celite and filtrate was reduced to 5 to 8 mL, affording colorless crystals of **6** overnight at –35 °C. Crystals of **6** used for the X-ray diffraction experiment were grown from a toluene solution.

^{1}H NMR (500 MHz, C_6D_6, 25 ^{o}C): δ 0.77 (s, 3H, CH_3), 1.03 (s, 18H, *t*Bu), 6.33 (s, 1H, Si-H), 6.95-6.77 (m, 5H, Ph) ppm.

^{13}C NMR (125.72 MHz, C_6D_6, 25 ^{o}C): δ 3.87 ($SiCH_3$), 31.06 (CMe_3), 54.66 (CMe_3), 127.89 (CN), 128.64, 129.85, 134.38, 138.23 (Ph), 170.69 (NCN) ppm.

^{29}Si{^{1}H}NMR (99.36 MHz, C_6D_6, 25 °C): δ -113.18 ppm.

M. P.: 116.4 °C.

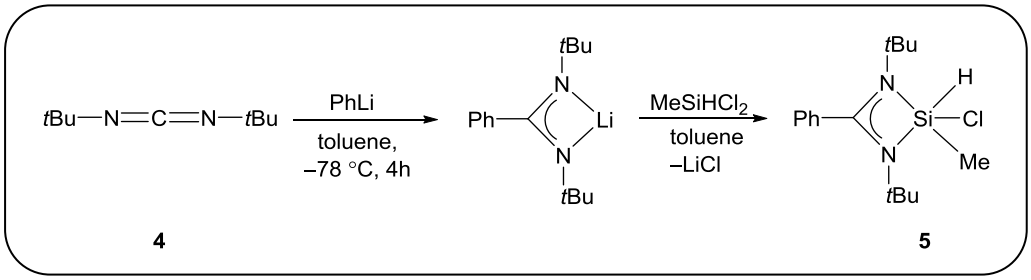
FT-IR (KBr, cm-1): υ 2189.70 (CN).

Anal. Cacld for $C_{17}H_{27}N_3Si$: C, 67.72; H, 9.03; N, 13.94. Found: C, 63.35; H, 8.48; N, 11.02.

4.4. Results and Discussions

4.4.1. Synthesis and characterization of catalyst 5

The compound **5** was synthesized by using the synthetic procedure, which has been utilized for the synthesis of ($PhC(NtBu)_2SiCl_3$)[20a] or ($PhC(NtBu)_2SiHCl_2$).[20b] The reaction of $MeSiHCl_2$ with *tert*-butyl carbodiimide **4** and phenyl lithium results in the formation of a neutral penta coordinate Si(IV) compound **5**, ($PhC(NtBu)_2SiH(CH_3)Cl$) (Scheme 1).



Scheme 1. Preparation of Catalyst **5**.

Compound **5** was crystallized in the orthorhombic space group with space group of $P2_1$ and the selected bond lengths and angles are provided in the legend of the Figure 1.[21] The compound **5** shows an approximate trigonal bipyramidal geometry at the central silicon atom, in which H1, N1, and C16 atoms occupy at the equitorial position and C1 and N2 situated on epical position. The bond length of Si–C bond is 1.849(8) Å, which is in good agreement with the previously reported Si–C single bonds.[22]

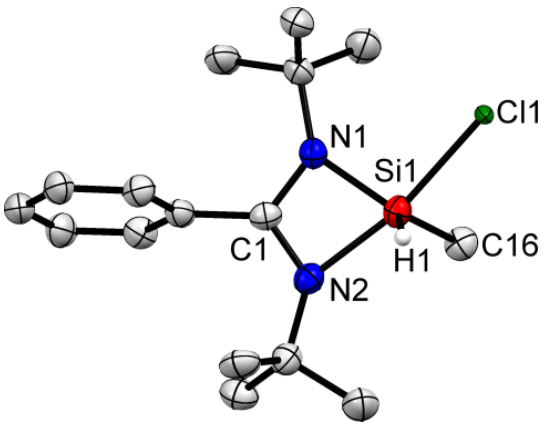
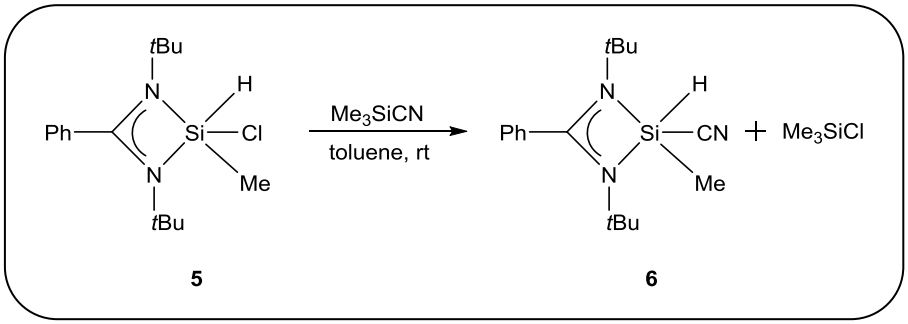


Figure 1. Molecular structure of **5**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms (except H1 bonded to Si1) are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Si1–H1 1.35(7), Si1–Cl1 2.365(2), Si1–C16 1.852(8); N1–Si1–C16 118.0(3), N2–Si1–N1 69.7(3), C16–Si1–N2 97.7(3), N1–Si1–Cl1 100.9(2), C16–Si1–Cl1 94.5(3), N2– Si1–Cl1 167.1(2).

The Si–H bond length is of 1.360(7) Å, which is marginally shorter than that of previously reported LSiCl(H)N(H)-N=CPh$_2$ [L = PhC(N*t*Bu)$_2$] [1.350 Å].[23] The ^{1}H NMR spectrum of **5** shows a signal at δ 6.33 ppm, which indicates that the formation of Si–H protons. In the ^{29}Si NMR spectrum, compound **5** shows a resonance at δ –80.66 ppm due to the five coordination at the central Si atom. The streching frequency of the Si–H bond in **5** detects at 2160.70 cm^{-1}. However, the molecular ion peak was found at *m/z* 310 with the highest relative intensity.

4.4.2. Synthesis and characterization of Int-1, 6

In order to understand the mechanism of cyanosilylation of aldehydes with TMSCN, we have performed a reaction between **5** and TMSCN at room temperature and suggests the possible formation [LSi(H)(CH$_3$)CN] **6** with the concomitant evolution of trimethylsilylchloride (Scheme 2).



Scheme 2. Formation of Int-1, **6**.

The formation of **Int-1** (**6**) was further confirmed by single crystal X-ray diffraction studies (Figure 2).[21] The structural features of **Int-1** (**6**) are similar to those in **5**.

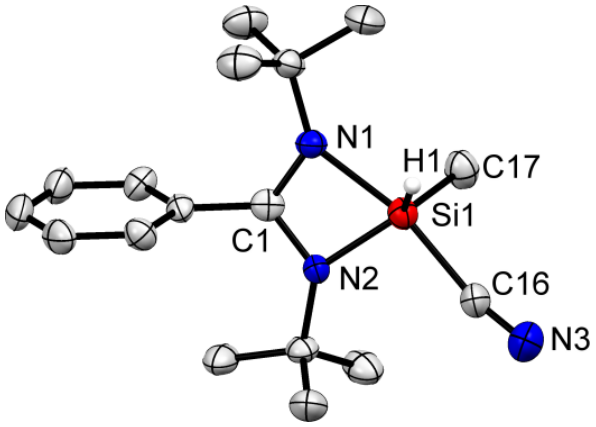


Figure 2. Molecular structure of **Int-1, 6**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms (except H1 bonded to Si1) are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Si1–H1 1.50(5), Si1–C16

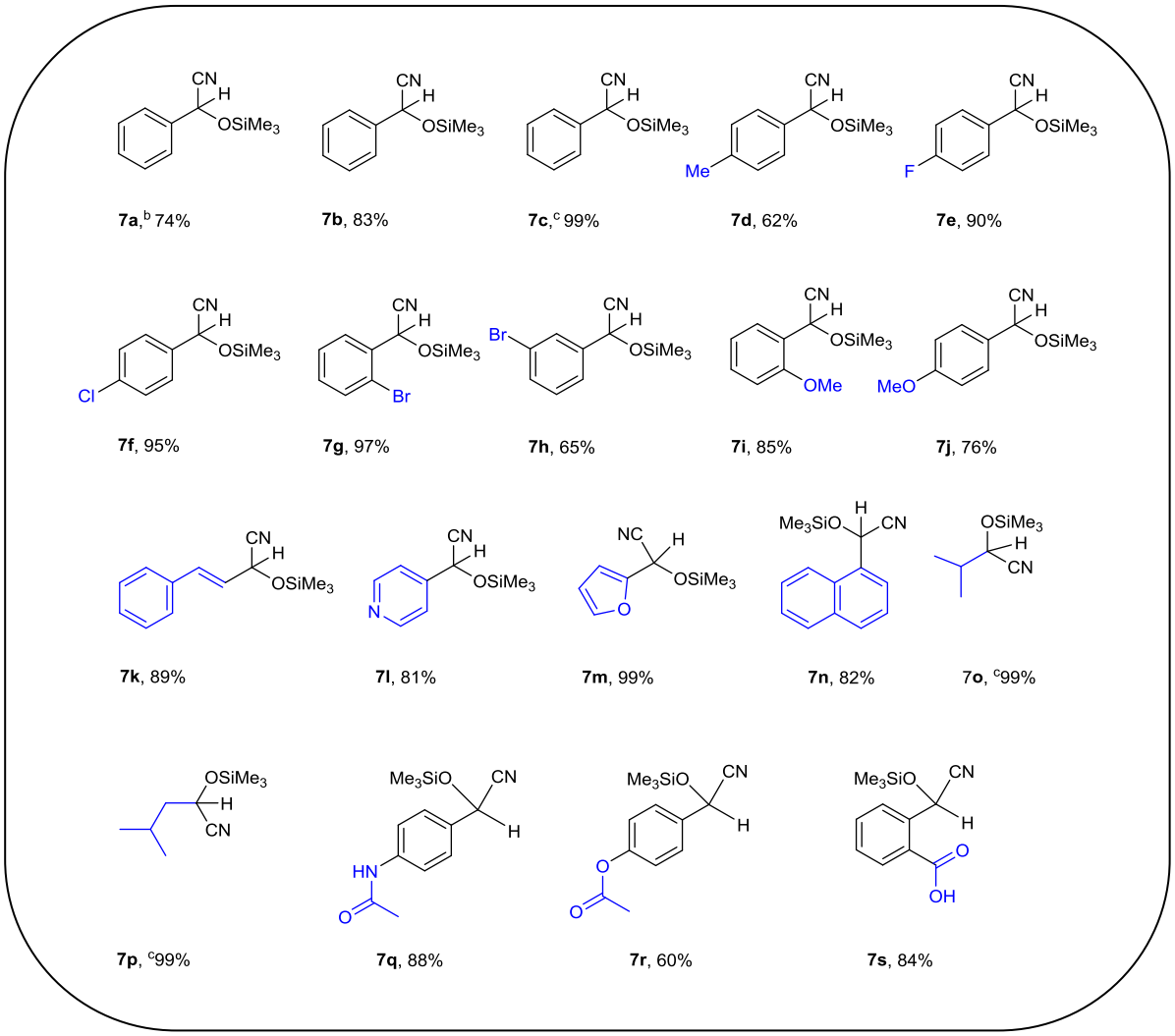
1.960(8), Si1–C17 1.845(7), Si1–N1 1.970(5), Si1–N2 1.802(5), C16–N3 1.15(1); N2–Si1–C16 99.3(3), N2–Si1–N1 69.2(2), N2–Si1–C17 119.6(3), C17–Si1–C16 94.8(3), C17–Si1–N1 97.0(3), C16–Si1–N1 166.6(3), Si1–C16–N3 168.5(7).

The central silicon atom of **6** shows distorted trigonal bipyramidal geometry. C17, N2, and H1 occupy the equatorial position whereas N1 and C16 reside at the axial position with an N1-Si1-C16 bond angle of 166.6(3)°. The bond length of Si–Me in 4.1 is [1.845(7) Å] similar to that of **5**. However, the bond length Si–H is 1.50(4) Å which has been increased in compared to that of **5** due to the more electropositive Si(IV) center. The Si–CN bond length is of 1.960(8) Å, which is longer than the usual Si–C single bond presumably due to the sp-hybridization of the C atom. The bond length of C≡N bond is 1.15(1) Å, which is in good agreement with the previously reported free isocyanides of C≡N bond length (1.14 to 1.16 Å).[24,25]

4.5. Application in Cyanosilylation of Aldehydes

We have initially tested the catalytic activity of **5** for the cyanosilylation of benzaldehyde with trimethylsilylcyanide at room temperature (Scheme 3). These studies demonstrated that the compound **5** is an efficient catalyst for the cyanosilylation of benzaldehyde with Me_3SiCN under mild reaction conditions, to afford the corresponding cyanosilylated product in 74% yield (Scheme; entry **7a**) taking 0.5 h with 2 mol% of the catalyst loading. However, this reaction does not take place without using the catalyst. Moreover, we have also tested the cyanosilylation of aldehydes using $MeSiHCl_2$ (10 mol%) as a catalyst in the place of **5** but no reaction was observed even after prolonged heating. Based on our catalytic observations, with 3 mol % catalyst and 6 hours reaction time, the yield of the reaction was increased to 83 % (entry **7b**) and with heating at 55 °C, the yield was up to 99 % (entry **7c**). As shown in Scheme 3, the reaction of aliphatic, aromatic, and hetrocyclic aldehydes with trimethylsilylcyanide in the presence catalyst **5** proceeded smoothly under optimal conditions of 3 mol% catalyst at room temperature with a 6 h reaction time. Aldehydes with electron-donating substituents (entry **7d**) were afforded the corresponding cyanosilylated products in moderate to good yield. Halogenated benzaldehydes can be exclusively cyanosilylated at the carbonyl functionality and no *σ*-bond metathesis reaction between the halogen moiety and Me_3SiCN was observed (entry **7e**-**7h**). Methoxy substituted benzaldehydes were gave the respective cyanohydrins (**7i** and **7j**). In case of *α,β*-unsaturated carbonyl such as cinnamaldehyde was selectively produced the 1,2-addition product regioselectively, without the formation of any 1,4-adductt (entry **7k**). 1-Naphthaldehyde (entry **7n**) and heteroaromatic

aldehydes such as pyridyl 4-carbaldehyde (entry **7l**) and 2-fulfuraldehyde (entry **7m**) were selectively gave their corresponding cyanohydrins in good to high yields under the regular conditions.



7a,[b] 74% **7b**, 83% **7c**,[c] 99% **7d**, 62% **7e**, 90%

7f, 95% **7g**, 97% **7h**, 65% **7i**, 85% **7j**, 76%

7k, 89% **7l**, 81% **7m**, 99% **7n**, 82% **7o**, [c]99%

7p, [c]99% **7q**, 88% **7r**, 60% **7s**, 84%

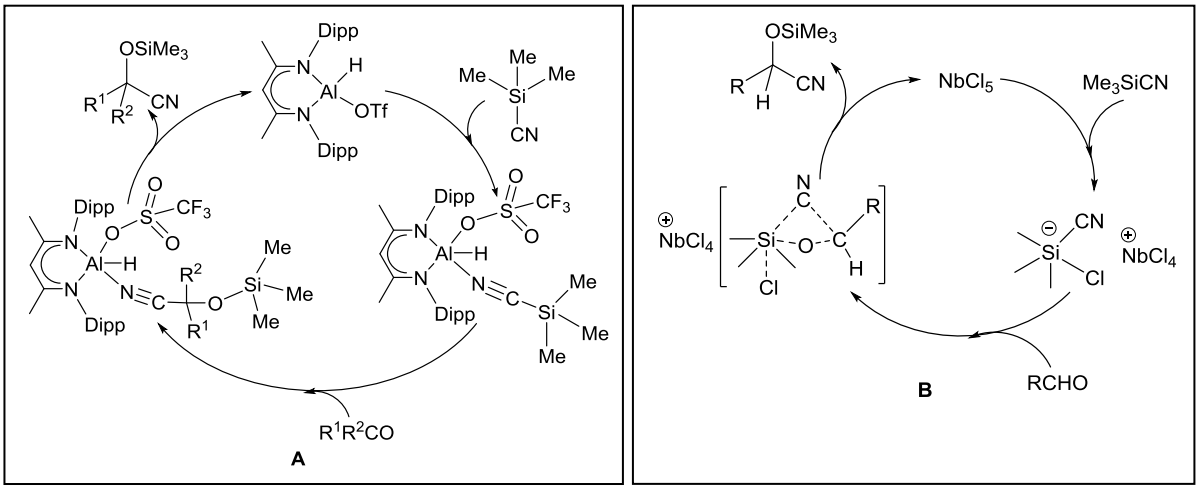
Scheme 3. [a]Reaction conditions: 3 mol% catalyst, 6h reaction at room temperature in benzene. Yields were determined by NMR spectroscopy on the basis of the consumption of the aldehyde. [b]2 mol% catalyst; [c]heating at 55 °C.

These suggest that the catalytic system selectively cyanated the carbonyl functionality and keeps the heterocycles intact. The reaction of aliphatic aldehydes with TMSCN afforded the corresponding cyanohydrins using 2 mol% catalyst and heating at 55 °C, giving good to excellent yields (entries **7o** and **7p**). Aldehydes were selectively and exclusively cyanosilylated in the presence of acid (entry **7s**), amide (entry **7q**) and ester (entry **7r**). In addition to this work, we also examined the scope of cyanosilylation for ketones. However, even after elevating the loading of catalyst, reaction temperature, time, and altering the

solvent did not lead to the formation of cyanohydrins of ketone. Similar to **1** and **3**, the cyanosilylation of ketones with TMSCN using **5** was misfired, which can be attributed to the higher coordination and sterics around the silicon atom.

4.6. Mechanistic Investigations

We have tried to investigate the reaction mechanism of the cyanosilylation of aldehydes. The groups of Yang, Parameswaran, and Roesky previously calculated the catalytic cycle for cyanosilylation of aldehydes and ketones by **3**. However, the proposed intermediates were not isolated.[1] Zhi et al. theoretically demonstrated that the initial step proceeds through the transfer of electron density from the N atom of the CN group to an elctrophilic aluminum center. In the next step, the reaction continues through the insertion of the C=O moiety into the Si–C bond of trimethylsilycyanide (Scheme 4, Mechanism **A**). However, the activation barrier was calculated to be 32kcal/mol.



Scheme 4. Mechanism **A** was proposed by Zhi, Parameswaran, and Roesky and their co-workers for the operation of the NacNacAlH(OTf) catalyst. Mechanism **B** was proposed by George and Kim for cyanosilylation of carbonyl compounds catalyzed by $NbCl_5$.

Moreover, this path way was difficult to accommodate a Lewis base on silicon center because the silicon center is already penta-coordinated. An alternative mechanism **B** was proposed by Kim and coworkers for the cyanosilylation of carbonyl compounds by $NbCl_5$ based on NMR studies. They reported that $NbCl_5$ reacts with Me_3SiCN to give hyper-valent silicate ions $[SiMe_3(CN)(Cl)]^-$, which subsequently reacts with the carbonyl group to give rise to the cyanosilylether. In connection with the mechanistic studies, the penta-coordinate silicon compound is of current interest as a catalyst. Corriu, Tacke, and others demonstrated that the

mechanism of R_3SiX compounds was initiated by the nucleophiles through the nucleophilic substitution at the silicon atom. [13e, 26] In order to investigate the reaction mechanism of aldehyde cyanosilylation, we have tried by NMR experiments. However, the 1:1 mixture of Me_3SiCN and the catalyst **5** in $CDCl_3$ at room temperature results in the development of a new $SiMe_3$ signal at δ 0.05 with simultaneous disappearance of the Me_3SiCN protons (δ 0.36 ppm) (see in Figure 3). Similarly, the new resonance at δ 5.29 ppm which is shifted upfield to that of **5**. The ^{29}Si-NMR spectrum of **6** shows a peak at δ –113.18 ppm usually suggests the five coordination of the silicon center, which is significantly high-field shifted with respect to that of **5**.

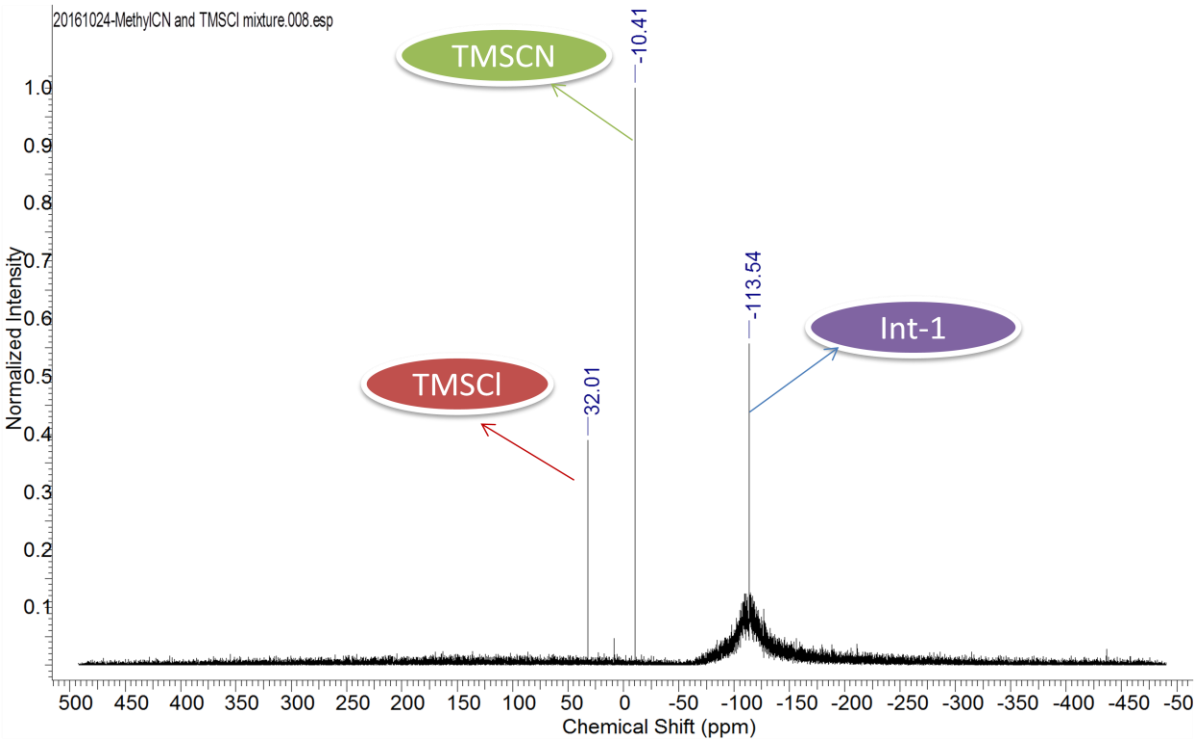
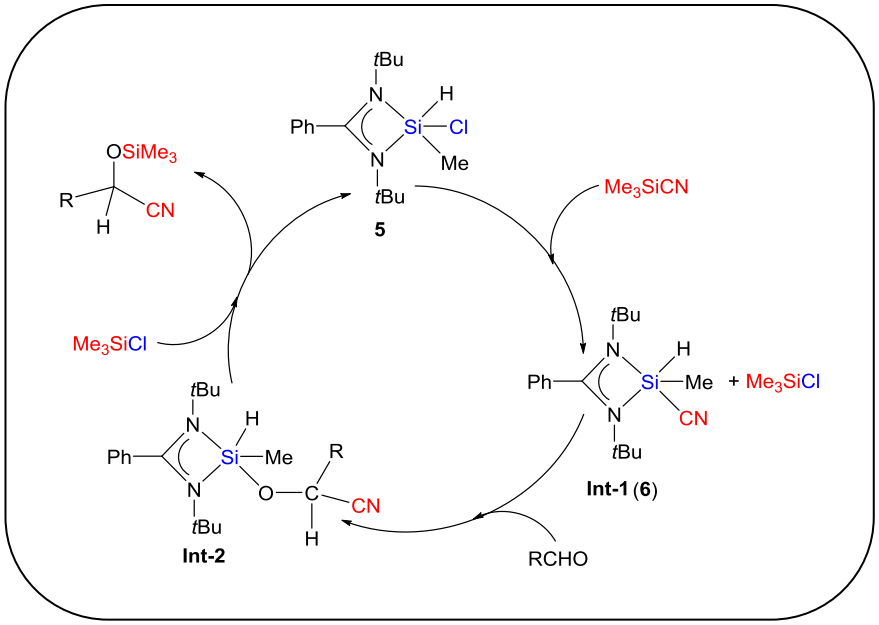


Figure 3. ^{29}Si NMR Spectroscopic proof for the formation of **6** (**Int-1**) and the liberation of Me_3SiCl

Hence, the possibility of silylium ion is ruled out, which usually detects in the downfield region.[27] Further, a new CN stretching band observed at 2189 cm^{-1} in the respective IR spectrum, which is completely different from the compound **5**.

Based on our keen observations by NMR experiments, plausible mechanism of cyanosilylation of aldehydes was showed by the use of catalyst **5** in Scheme 5. However, the reaction mechanism proceeded *via* σ-bond metathesis reaction between **5** and Me_3SiCN along with the evolution of Me_3SiCl, which resulted in the formation of an **Int-1**(**6**). The Si–CN

bond in **Int-1** (**6**) contains a long Si–CN bond and the N(amidinate)→Si bond diminishes the electrophilicity of the Si atom and raises the cleavage tendency of the Si–CN bond. Consequently, **Int-1** (**6**) further reacts with aldehydes to result in the alkoxy derivative **Int-2** with the concomitant migration of the CN substituent from the Si atom to the C atom. The driving force of this step may be due to the generation of Si–O bond in **Int-2**. In fact, Nagendran and co-workers have also demonstrated the analogous reaction between [LGeCN] (L=aminotroponiminate) and aldehydes that afforded the respective germylene alkoxide derivatives.[14]



Scheme 5. Proposed mechanism of cyanosilylation of aldehydes.

We have also carried out the NMR tube reaction between **Int-1** (**6**) and benzaldehyde at room temperature which indicates the formation of **Int-2** along with few undesired product. The formation of **Int-2** was studied by ^{1}H NMR, where a new signal appeared at δ 5.11 ppm while the Si–H proton shows a resonance at δ 6.24 ppm. The proton-coupled ^{29}Si NMR spectrum shows a new doublet resonance (δ -70.87 and -74.21 ppm) with a coupling constant of *J*Si-H = 265.5 Hz. All these data suggest the formation of **Int-2** during the catalytic cycle but unfortunately, we could not gain a pure spectrum even after several attempts. Finally, there is a σ-bond metathesis reaction between alkoxide derivatives and Me_3SiCl to result in the formation of cyanosilylated products and regeneration of the catalyst.

4.7. Conclusions

In summary, we have synthesized amidinato-supported methylsilane **5** in a single step. The compound **5** was well characterized and utilized as catalyst for the cyanosilylation of aldehydes with TMSCN at ambient conditions. We have also carried out the spectroscopic studies to understand the reaction mechanism of aldehyde cyanosilylation. However, the first step of the catalytic cycle proceeds through the nucleophilic substitution at the silicon center of **5**, leading to the formation of $(PhC(N\textit{t}Bu)_2SiH(CH_3)CN)$ **6** and the formed compound was structurally characterized. As the elimination of halosilane kicks start the catalytic cycle, this approach will motivate to use halogenated silicon compounds as catalysts for other important organic transformations.

4.8. References

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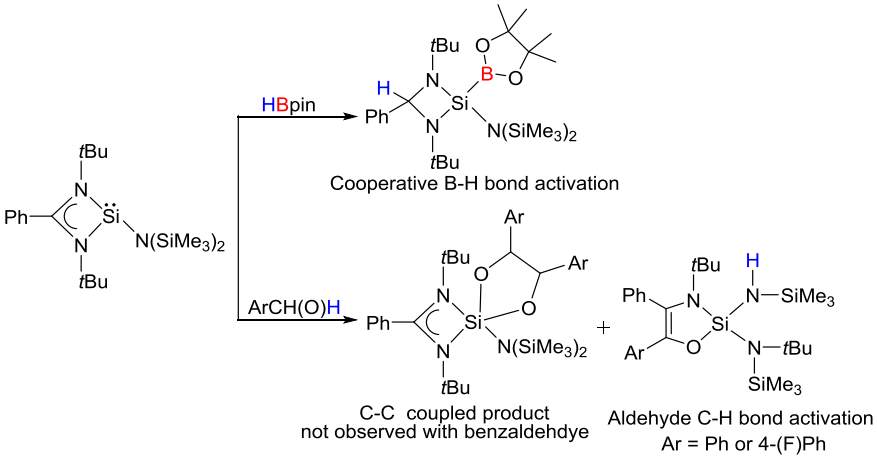
Silylene Induced Cooperative B–H and Aldehyde C–H Bond Activation and Subsequent Use as Single-site Hydroboration and Cyanosilylation Catalyst



Abstract

This chapter demonstrates the stoichiometric reactions of a stable silylene, [PhC(N*t*Bu)$_2$SiN(SiMe$_3$)$_2$] **7** with aldehyde and pinacolborane (HBpin) at room temperature. The addition of HBpin to **7** results in cleavage of the B–H bond through addition across the Si and amidinate-C sites in a cooperative fashion. Subsequent DFT calculations revealed that the reaction is thermodynamically and kinetically feasible at room temperature. The reaction of **7** with benzaldehyde led to the aldehyde C–H bond activation along with amidinate ring expansion, leading to a five-membered heterocycle. In case of 4-fluorobenzaldehyde, a C–C bond coupling takes place leading to a dioxasilolane derivative as the major product. Inspired by these findings, we reasoned that **7** would be excellent catalyst for the hydroboration of carbonyl compounds with pincaolborane. In addition, the catalytic application of **7** is extended for the addition of trimethylsilylcyanide to the aldehydic carbonyl group.

5.1. Introduction

The splitting of a B–H bond is well-known with transition metals both via oxidative addition[1] and, of late, by metal–ligandcooperativity.[2–6] The latter concept has only come to light in the past few years through the studies from the groups of Ostreich **1**,[2] Love **2**,[3] Iluc **4**,[4] Gessner **3**,[5] and others[6] (Chart 1). In a subsequent feature article, Feichtner and Gessner have summarized the recent developments on the use of transition metal carbene complexes in cooperative bond activation reactions.[7] The cooperative bond activation in main group chemistry is the area of mainly frustrated Lewis pairs and the B–H bond activation of HBcat using FLP, [*t*Bu$_2$RP (R = *t*Bu, 2-C$_6$H$_4$(C$_6$H$_5$)) and B(C$_6$F$_5$)$_3$] has been studied.[8] Apart from FLP, *c*AAC induced B−H bond activation has been examined by Bertrand's group, but it is the 1,1 oxidative addition,[9] and not the cooperative activation.

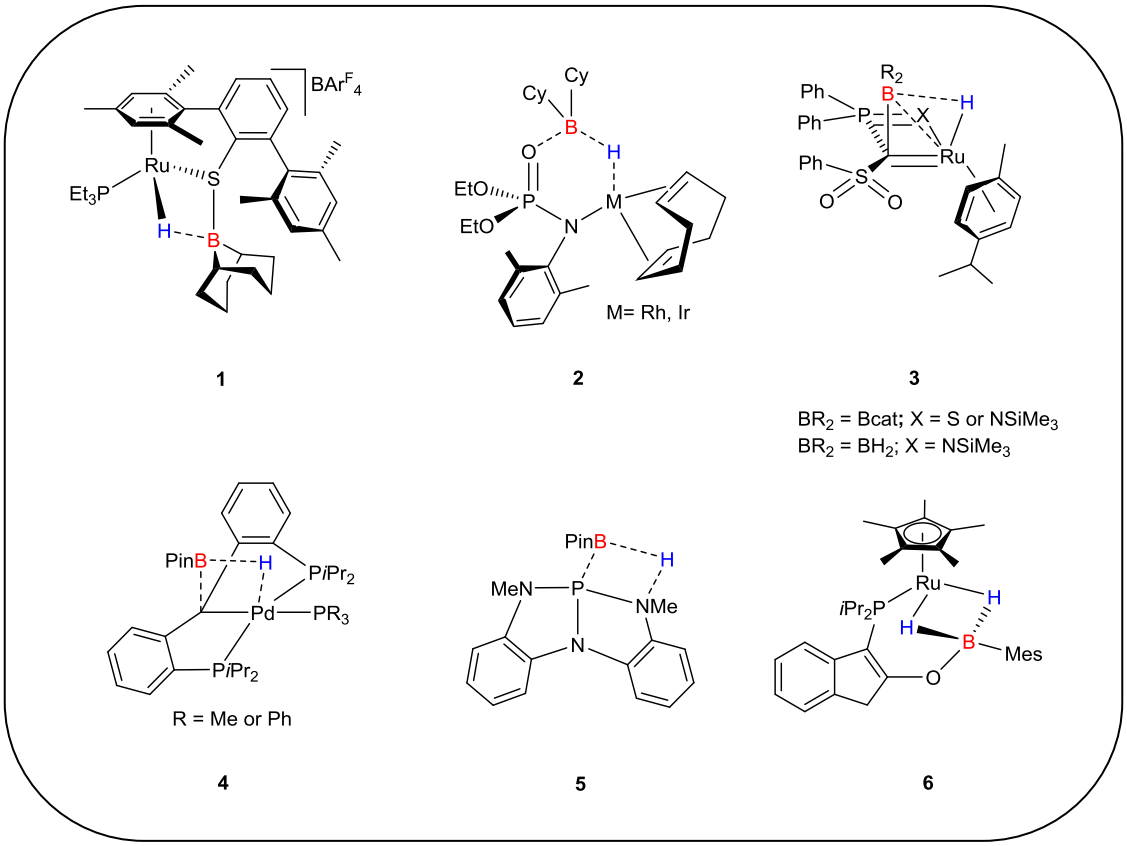


Chart 1. Selective examples of cooperative B–H bond activation with single component systems.

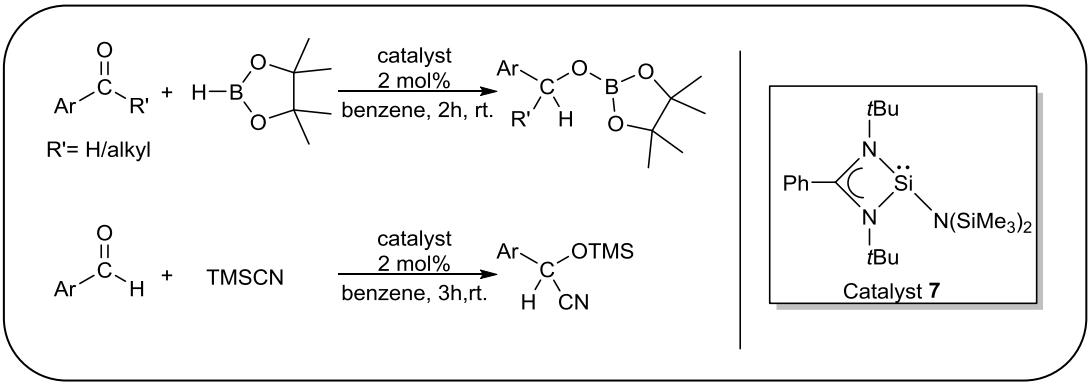
Very recently, Radosevich and coworkers demonstrated the first single-component system, which is capable of activating the B−H bond of HBpin in a cooperative fashion across to a P−N bond and to give the prodcut **5**.[10a] Stradiotto and coworkers

(Chart 1; **6**) have showed that [Ru]–O bond undergo B–H bond capture of H_2BMes (Mes = 2,4,6-trimethylphenyl).[10b] Ge(II), Al(III), Ga(III) compounds based on nacnac ligands with an exocyclic double bond are ambiphilic and have been found to undergo cooperative H–X bond activation.[11-13] Berben and coworkers have utilized a pincer-based aluminium complex, which activates the N–H bond and O–H bonds *via* metal–ligand cooperation.[14,15]

5.2. Objectives

The use of a silylene as a transition metal free catalyst for organic reactions remains a holy grail in contemporary main group chemistry.[16] Silylenes have shown remarkable ability towards small molecule activation,[17] which is one of the important reactions of transition-metal complexes because such activation is a key step of a catalytic cycle. The catalytic chemistry of silylene is restricted only as ligands for NHSi-transition metal complexes, which have been used in Heck or Suzuki type coupling, alkyne cyclotrimerisation, ketone hydrosilylation, amide reduction, or Sonogashira cross-coupling reactions.[18] Therefore, a major goal of silylene chemistry has been to push the limits of silylene as a single component catalyst through the construction of a catalytic cycle.

Recently, we have demonstrated the amidinato stabilized Si(IV) compound as a transition metal free catalyst for the hydroboration and cyanosilylation of a variety of aldehydes and ketones at ambient conditions.[19] In contrast, Si(II) compounds have remained little used in catalysis. Inspired by this facile cooperative activation of both aldehyde C–H and B–H bond, we considered the possibility of hydroboration with silylene, **7** as a single site catalyst (Scheme 1). Furthermore, **7** is an efficient catalyst for the aldehyde cyanosilylation at room temperature.



Scheme 1. S(II) catalyzed hydroboration of carbonyl compounds and cyanosilylation of aldehydes.

5.3. Experimental Section

All manipulations were performed using standard inert atmosphere glove box and Schlenk techniques. Solvents were dried and purified by MBRAUN solvent purification system MB SPS-800. Benzene was dried and distilled over Na/benzophenone mixture prior to use. The starting material, [PhC(N*t*Bu)$_2$SiN(Si(CH$_3$)$_3$)$_2$] **7** was prepared according to the literature procedures. pinacolborane, benzaldehyde and 4-fluorobenzaldehyde were purchased from Sigma Aldrich and TCI Chemicals, respectively. They were used without further purification. ^{1}H, ^{13}C, ^{29}Si and ^{19}F NMR spectra were recorded in $CDCl_3$ or C_6D_6 employing a Bruker Avance DPX 200, Bruker Avance DPX 400 or a Bruker Avance DPX 500 spectrometer referenced to external $SiMe_4$, in the case of ^{1}H, ^{13}C and ^{29}Si NMR and $CFCl_3$ for the ^{19}F NMR spectra, respectively. Elemental analysis was performed. Furthermore, Melting points were measured in a sealed glass tube on a Stuart SMP-30 melting point apparatus.

5.3.1. Synthesis of 8

To the solution of **7** (0.2 g, 0.47 mmol in 10 mL toluene), pinacolborane (0.06 g, 0.47 mmol in 10 mL toluene) was added at room temperature and the reaction mixture was stirred for 3 hours. Then the solvent was removed under reduced pressure and extracted with toluene (15 mL). The toluene solution was then concentrated (4 mL) and placed at -30 °C in a refrigerator for 2 days, affording colorless, X-ray quality crystals of **8** in 90.7% yield.

^{1}H NMR (400.31 MHz, $CDCl_3$, 25 ^{o}C): δ 0.42 (s, 18H, $SiMe_3$), 0.99 (s, 18H, *t*Bu), 1.31 (s, 12H, pinCH_3), 7.17-7.24 (m, 5H, Ph) ppm.

^{13}C NMR (100.67 MHz, $CDCl_3$, 25 ^{o}C): δ 6.44 ($SiMe_3$), 25.92 (PinCH_3), 30.83 (*t*Bu), 50.74 (C*t*Bu), 73.46 (CH), 83.41(OC(CH$_3$)$_2$), 127.26, 128.39, 129.97, 141.73, 147.65 (Ph) ppm.

^{29}Si{^{1}H} NMR (79.53 MHz, $CDCl_3$, 25 °C): δ -52.41 (SiN($SiMe_3$)$_2$), 3.13 (N($SiMe_3$)$_2$) ppm.

^{11}B NMR (128.44 MHz, $CDCl_3$, 25 ^{o}C): δ 37.84 ppm.

HRMS (m/z): calcd: 547.36, found: 547.3611.

M. P.: 133.6 °C.

Elemental analysis (%) calcd for $C_{27}H_{54}BN_3O_2Si_3$ (547.81): C, 59.20; H, 9.94; N, 7.67. Found: C, 58.98; H, 9.63; N, 7.88.

5.3.2. Synthesis of 9

The toluene solution (15 mL) of **7** (0.2 g, 0.47 mmol) was added drop by drop to the toluene solution (10 mL) of benzaldehyde (0.05 g, 0.47 mmol) at ambient conditions. The reaction was monitored by NMR spectroscopy which indicates after 12 hours the formation of a product. The solution was removed under reduced pressure and extracted with toluene (12 mL). The toluene solution was then concentrated (5 mL) and placed at -30 °C in a freezer for 3 days, affording colorless, X-ray quality crystals of **9** in 72% yield.

^{1}H NMR (400.31 MHz, C_6D_6, 25 ^{o}C): δ 0.32 (s, 9H, $SiMe_3$), 0.43 (s, 9H, $SiMe_3$), 1.27 (s, 9H, *t*Bu), 1.46 (s, 9H, *t*Bu), 4.93 (brs, 1H, NH), 6.96-7.04 (m, 5H, Ph), 7.12-7.14 (m, 5H, Ph) ppm.

^{13}C NMR (100.67 MHz, C_6D_6, 25 ^{o}C): δ 2.51 ($SiMe_3$), 8.00 ($SiMe_3$), 33.19 (*t*Bu), 33.82(*t*Bu), 53.54 (C*t*Bu), 55.56 (C*t*Bu), 124.69, 142.46 (C=C), 128.53, 130.62, 131.07, 133.40, 133.61, 133.71, 134.07, 135.92, 137.61, 140.93 (Ph) ppm.

^{29}Si{^{1}H}NMR (79.53 MHz, C_6D_6, 25 °C): δ -39.48 ($SiN(SiMe_3)_2$), 1.47, 2.18 ($N(SiMe_3)_2$) ppm.

HRMS (ESI, m/z): calcd: 525.95, found: 526.3100 $[M+H]^+$.

Elemental analysis (%) calcd. for $C_{28}H_{47}N_3OSi_3$ (525.96): C, 63.94; H, 9.01; N, 7.99. Found: C, 63.61; H, 8.82; N, 8.12.

5.3.3. Synthesis of 10 and 11

The toluene solution (10 mL) of 4-fluorobenzaldehyde (0.059 g, 0.47 mmol) was added drop by drop to the toluene solution (10 mL) of **7** (0.2 g, 0.47 mmol) at room temperature. The reaction mixture was slowly turned from yellow to colorless. After six hours, the ^{1}H NMR spectrum was recorded and indicated the formation of two products. The solution was removed under reduced pressure and extracted with toluene (10 mL). The toluene solution was then concentrated (5 mL) and placed at room temperature for 7 days, affording colorless, X-ray quality crystals of **10** (63.1% yield) in major fraction along with the formation of minor product **11** (8% yield).

Spectroscopic information for 10: ^{1}H NMR (400.31 MHz, C_6D_6, 25 °C): δ 0.33 (s, 9H, $SiMe_3$), 0.44 (s, 9H, $SiMe_3$), 1.28 (s, 9H, *t*Bu), 1.47 (s, 9H, *t*Bu), 6.61-6.66 (m, 2H, CHCH),

7.01-7.04 (dd, 4H, Ph), 7.10-7.14 (m, 5H, Ph), 7.30-7.33 (d, 2H, Ph), 7.52-7.55 (d, 2H, Ph) ppm.

^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 2.48 ($SiMe_3$), 7.97 ($SiMe_3$), 33.15 (*t*Bu), 33.81 (*t*Bu), 53.53 (C*t*Bu), 55.55 (C*t*Bu), 114.68 (CHCH), 114.89 (CHCH), 126.09, 126.17, 128.48, 128.59, 128.65, 130.09, 130.11, 130.35, 137.43, 140.94, 153.02, 159.49 (Ph), 161.91 (NCN) ppm.

^{19}F NMR (376.63 MHz, C_6D_6, 25 °C): δ -118.93 (s, 1F, Ar−F), -118.99 (s, 1F, Ar−F) ppm.

^{29}Si{^{1}H}NMR (79.53 MHz, C_6D_6, 25 °C); δ -38.17 ($SiN(SiMe_3)_2$), 2.88, 3.49 ($N(SiMe_3)_2$) ppm.

HRMS (ESI, m/z): calcd: 668.05, found: 668.3330 $[M+H]^+$.

Elemental analysis (%) calcd. for $C_{35}H_{52}F_2N_3O_2Si_3$ (668.05) C, 62.83; H, 7.83; N, 6.28. Found: C, 56.75; H, 7.11; N, 5.46.

Spectroscopic information for 11: ^{1}H NMR (400.31 MHz, C_6D_6, 25 °C): δ 0.32 (s, 9H, $SiMe_3$), 0.44 (s, 9H, $SiMe_3$), 1.28 (s, 9H, *t*Bu), 1.47 (s, 9H, *t*Bu), 4.90 (brs, 1H, NH), 6.61-6.65 (m, 2H, Ph), 7.00-7.13 (m, 5H, Ph), 7.13 (d, 1H, Ph), 7.53 (d, 1H, Ph) ppm.

^{19}F NMR (376.63 MHz, C_6D_6, 25 °C): δ -118.96 (s, 1F, Ar−F) ppm.

HRMS (ESI, m/z): calcd: 543.95, found: 544.3005 $[M+H]^+$.

5.3.4. Synthesis of 12

The toluene solution of **7** (0.2 g, 0.47 mmol) was cooled to –60 °C under inert conditions and pinacolborane (0.06g, 39.02 mmol) was added dropwise over a period of five minutes. The suspension was stirred for the next 40 minutes and 4-fluorobenzaldehyde (0.058g, 0.47 mmol) was added dropwise over a period of 10 minutes at –60 °C. The reaction mixture was slowly turned from yellow to colorless when allowed to warm at room temperature for 20 minutes. The solvent was removed under reduced pressure and extracted with toluene (10 mL) which was reduced *in vacuo* to 5 mL and kept at room temperature for 3 days to obtain colorless crystals of **12** in 69.7% yield.

^{1}H NMR (400.31 MHz, C_6D_6, 25 °C): δ 0.64 (s, 18H, $SiMe_3$), δ 1.00 (s, 12H, *pin*(Me)), 1.19 (s, 18H, *t*Bu), 5.36 (d, J = 4.40 Hz, 1H, CH), 5.57 (d, J = 4.40 Hz, 1H, SiH), 6.79-6.91 (m, 5H, Ph), 7.00-7.03(d, 2H, Ph), 7.64-7.67 (d, 2H, Ph) ppm.

^{13}C NMR (100.67 MHz, C_6D_6, 25 °C): δ 5.91 ($SiMe_3$), 24.48, 25.15 ($SiMe_3$), 32.89 (*t*Bu), 55.51 (C*t*Bu), 69.98 (CH), 115.11, 126.38, 127.62, 127.99, 128.08, 131.47, 139.02, 140.00, 153.01, 160.71 (Ph),, 163.59 (NCN) ppm.

^{13}C-DEPT NMR (100.67 MHz, C_6D_6, 25 ^{o}C): δ 5.59 ($SiMe_3$), 24.16, 24.83 (Me), 32.58 (*t*Bu), 69.66 (CH), 114.90, 126.46, 127.69, 128.16, 130.28, 131.08, 131.16, 133.28 (Ph) ppm.

^{19}F NMR (376.63 MHz, C_6D_6, 25 °C): δ -115.47 (s, 1F, Ar−F) ppm.

^{29}Si{^{1}H}NMR (79.53 MHz, C_6D_6, 25 °C): δ -27.70 ($SiN(SiMe_3)_2$), 9.05 ($N(SiMe_3)_2$) ppm.

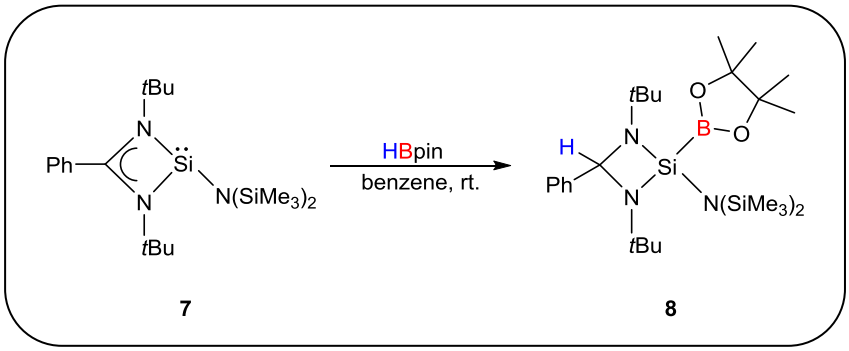
^{11}B NMR (128.44 MHz, C_6D_6, 25 ^{o}C): δ 20.55 (C(O)Bpin) ppm.

HRMS (ESI, *m/z*): calcd: 671.39, found: 672.40 $[M+H]^+$.

5.4. Results and Discussions

5.4.1. Synthesis and characterization of 8

Due to our current interest in hydroboration chemistry,[20,19a] we commenced our study by stoichiometric reactions of $PhC(NtBu)_2SiN(SiMe_3)_2$ (**7**)[21] with both aldehydes and pinacolborane (HBpin). Recently, Mézailles and coworkers demonstrated that the activation of the B-H bond relies upon the ambiphilic character of the substrate.[22] Bertrand and coworkers reported the 1,1-addition of the B–H bond of HBpin at *c*AAC carbene.[9] Similar to *c*AAC, silylenes are less nucleophilic and more electrophilic than typical NHCs, and hence are tailor-made for such activation. Recently, So and co-workers studied the reactivity of silylene towards BH_3, which initially led to the adduct formation and consequently insertion of the B-H bond into the Si-N bond.[23] In marked contrast, the addition of HBpin to **7** resulted in cleavage of the B–H bond of HBpin through addition across the Si(II) and amidinate carbon center in a cooperative fashion (Scheme 2). According to NMR spectroscopy, the reaction of **7** with HBpin showed a new resonance at δ 5.04 ppm with simultaneous disappearance of HBpin (q, BH, δ 2-3 ppm) resonances. This new resonance corresponds to the aliphatic CH proton, and thereby indicating the formation of a cyclic four membered diamido Si(IV) compound. The ^{13}C NMR spectrum of **8** appears at δ 73.46 ppm for the CH carbon. The four coordination of silicon atom is reflected from the resonance at δ -52.41 ppm in the ^{29}Si NMR spectrum. The ^{11}B NMR spectrum shows a new resonance at δ 37.84 ppm, indicating the Si–B bond formation.



Scheme 2. Cooperative B–H bond activation of HBpin with silylene **7**.

Colorless crystals of **8** suitable for single crystal X-ray structural analysis were grown from a saturated toluene solution at -32 °C in two days. **8** crystallizes in the orthorhombic space group *Pbca* and the molecular structure is depicted in Figure 1.

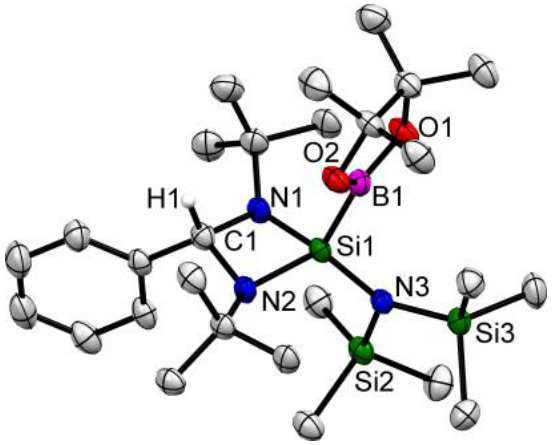


Figure 1. Molecular structure of **8**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms (except H1 bonded to C1) are omitted for clarity. Selected bond distances (Å) and bond angles (deg): C1–H1 1.00(5), Si1–B1 2.031(5), Si1–N1 1.743(3), Si1–N2 1.742(3), Si1–N3 1.740(4); N1–Si1–B1 109.8(2), N2–Si1–B1 114.4(2), N3–Si1–B1 113.2(2), N1–Si1–N2 77.4(2), N1–Si1–N3 120.1(2).

The silicon atom is bound to three nitrogen atoms (two from the amidinato ligand and one from the amide substituent moiety), and one boron atom, and exhibits a distorted tetrahedral geometry. The formation of diamido ligand is reflected from the shortening of the Si–N bond lengths (1.743(3) and 1.742(3) Å) than those from Si–$N_{amidinate}$ ligands (1.769(7) and 1.878(1) Å).[21] The Si1–B1 bond length is of 2.027(6) Å, which is in good agreement with the Si–B bond length in Aldrich's $\{B(NArCH)_2\}\{N(SiMe_3)Ar\}SiH_2$ (2.016(2) Å) (Ar = 2,6-*i*Pr_2-C_6H_3)[24] and Braunschweig's silaborinines (1.9899(15) and 2.019(3) Å).[25]

5.4.2. DFT compoutations for 8

We have also investigated the mechanism of the B–H bond activation by **7** with help of DFT studies.

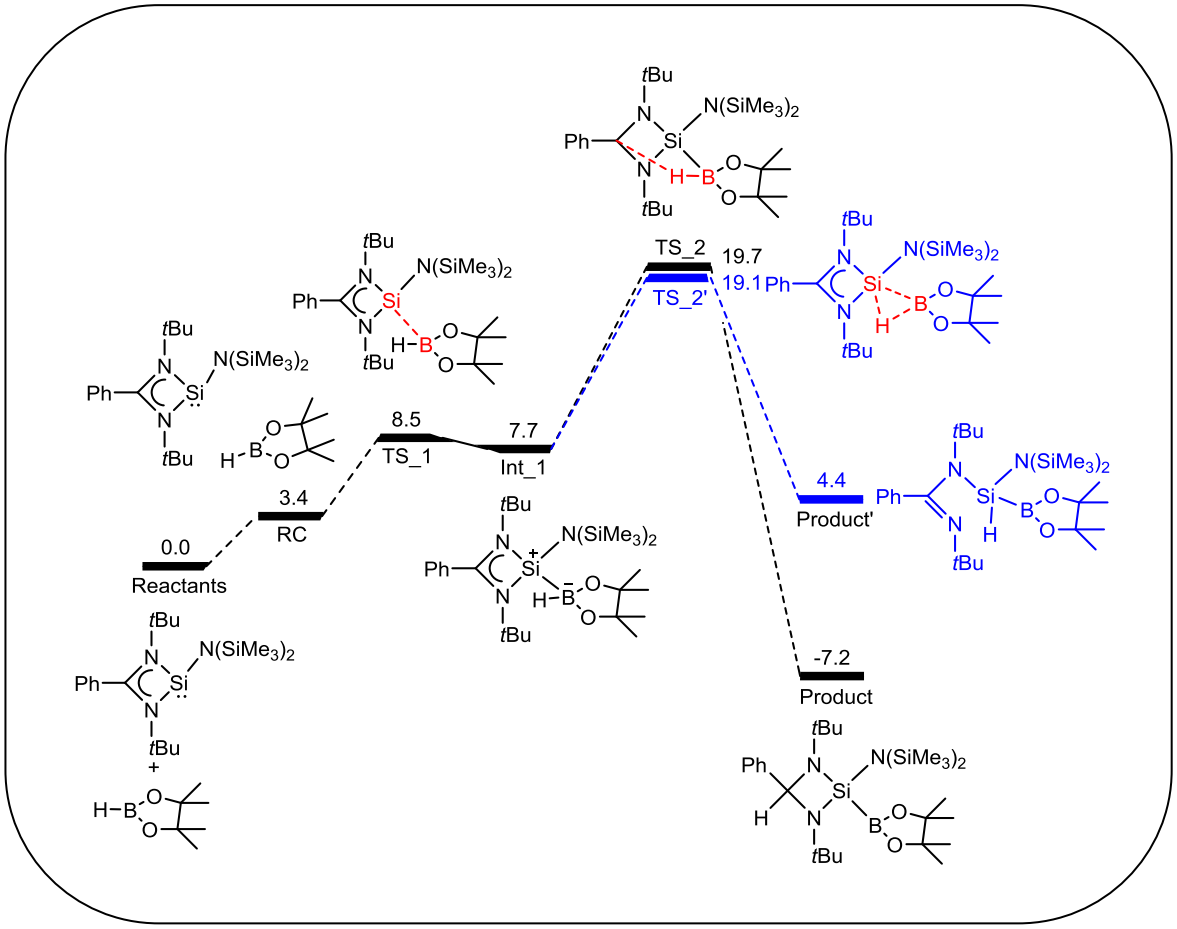


Figure 2. The reaction free energy profile diagram for the B-H bond activation by **7**. The values (in kcal/mol) have been calculated at the PBE/TZVP level of theory.

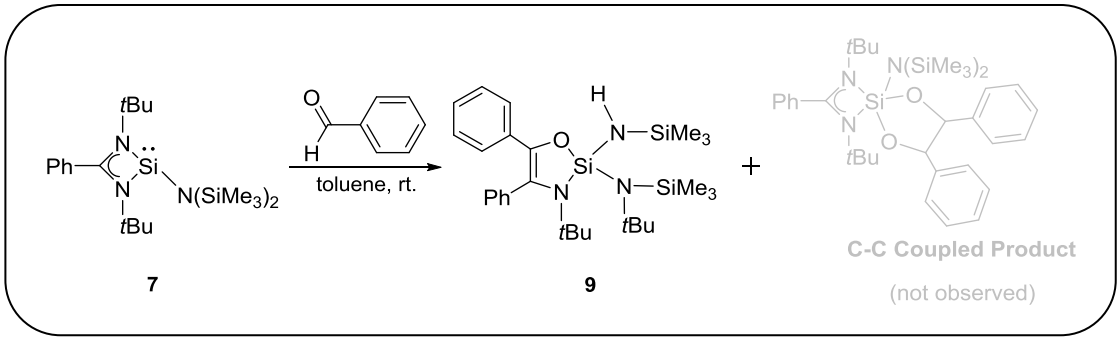
The reaction mechanism initially continues through a transition state **TS_1**, with the corresponding energy barrier of 8.5 kcal/mol, in which the Si–B bond is formed due to the transfer of electron density from silicon to the vacant orbital of boron, which leads to an intermediate **Int_1** (Figure 2). Then, the reaction further proceeds through a second transition state **TS_2,** with an energy barrier of 19.7 kcal/mol, in which the transfer of a hydride ion from boron to carbon and which leads to a thermodynamically stable (-7.2 kcal/mol) product. Therefore, the DFT calculations suggest that splitting of a B–H bond by **7** is thermodynamically and kinetically feasible at room temperature. The viability of formation of a product arising from 1,1 oxidative addition at the silicon center (three membered transition state) was also calculated. Even though the oxidative addition is kinetically viable

(barrier: 19.1 kcal/mol), the product is thermodynamically unfavourable by 11.6 kcal/mol with respect to **8**.

5.4.3. Synthesis and characterization of 9

Subsequent to the B–H bond activation of HBpin, we have moved towards the reaction of aldehydes with **7** to explore the possibility to apply such stoichiometric reactivity to catalysis. The C–H bond activation of aldehydes has been demonstrated by late transition metals.[26] Whether the low valent main group element compounds can compete this reactivity is remained to be seen. The reactions of **7** with benzaldehyde and 4-fluorobenzaldehyde led to the C–H bond activation accompanied by amidinate ring expansion with the formation of a five-membered heterocycle. While ring expansion chemistry of *N*-heterocyclic carbenes is undergoing a great surge,[27] related chemistry of N-heterocyclic silylene is relatively cursory. Braunschweig and coworkers have studied the ring expansion of West's silylene (NHSi) upon reaction with $PhBX_2$ (X = Cl, Br) to give six-membered silaborinines.[25]

The reactions between silylenes and ketones are well established.[28] In marked contrast, the reported reactions of silylenes with aldehydes are very rare in the literature. To our knowledge, there is only reaction of a stable silylene with an aldehyde was studied by Jutzi et al. in 1996 which led to a product with a C–C bond formation leaving the C–H moiety intact.[29] The reaction of **7** with benzaldehyde afforded the activation C–H bond the activation product along with formation of ring expansion (Scheme 3). This is quite unusual as the ring expansion usually requires a hydride source.[27,23]



Scheme 3. Reaction of **7** with benzaldehyde.

The formation of **9** was corroborated by single crystal X-ray diffraction studies (Figure 3). Mechanistically we can propose that the benzoyl moiety was inserted into the C–N bond resulting in the formation of a C–C double bond. Besides, one of the $SiMe_3$ groups migrates to another N atom bound to the *t*Bu group and the hydride binds to the N atom bound to another $SiMe_3$.

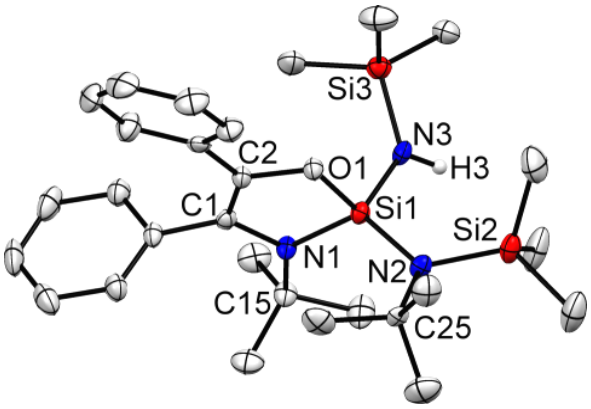


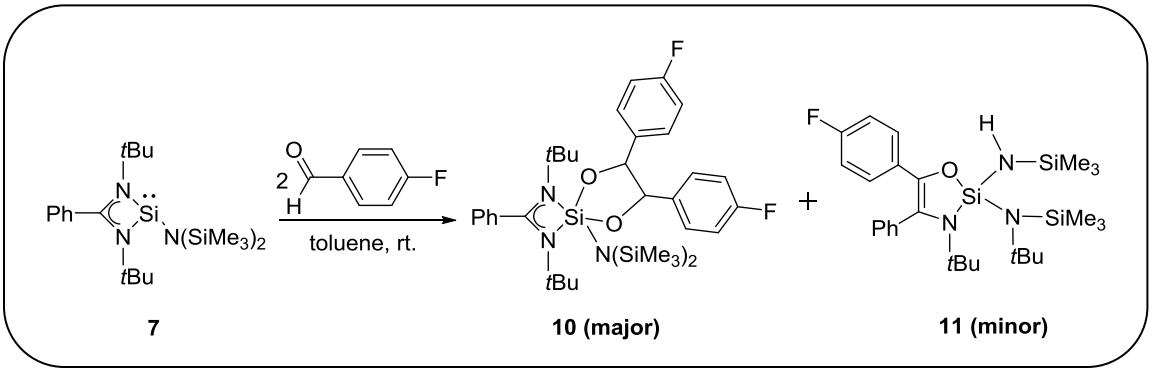
Figure 3. Molecular structure of **9**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms (except H3 is bonded to N3) are omitted for clarity. Selected bond distances (Å) and bond angles (deg): C1–C2 1.347(4), C2–O1 1.394(4), Si1–O1 1.650(2), Si1–N1 1.745(2), C1–N1 1.419(4), Si1–N2 1.714(3), Si1–N3 1.697(2), Si3–N3 1.725(2), Si2–N2 1.767(3); O1–Si1–N1 92.90(1), N1–Si1–N2 119.90(1), N1–Si1–N3 113.50(1), O1–Si1–N2 113.20(5), O1–Si1–N3 106.10(1), C1–N1–Si1 108.10(2), C2–O1–Si1 112.20(2), C1–C2–O1 113.40(3), N1–C1–C2 113.30(3), H3–N3–Si1 116.10(0), Si1–N2–Si2 118.80(1).

The silicon atom is bound to three nitrogen atoms, and one oxygen and adopts a distorted tetrahedral geometry. The bond lengths of Si–N are (~1.718 Å) slightly longer than the Si–N single bonds of **8** (~1.727 Å). The C1–C2 bond length is of 1.345(4) Å, which is comparable to double bond formation between C1 and C2. This is further confirmed by the ^{13}C NMR spectrum where the appearance of two new signals at δ 124.69 and 142.46 ppm corresponds to C1 and C2. The ^{1}H NMR spectrum of **10** displays a broad resonance at δ 4.93 ppm for N–H proton. A resonance at δ –39.48 ppm in the ^{29}Si NMR indicates the four-coordination at the central silicon atom. Interestingly, we did not see the formation of any 1, 3 -dioxasilolane derivative even when altering the molar ratio of the reaction partners.

5.4.4. Synthesis and characterization of 10 and 11

We have chosen 4-fluorobenzaldehyde as a substrate to react with **7**. The reaction has three possible consequences: (i) activation of C–F bond with silylene,[30,31] (ii) activation of aldehyde C–H bond and subsequent ring expansion (*vide supra*), and (iii) the C–C coupling reaction as reported by Jutzi et al.[29] The reaction afforded the 1,3-dioxasilolane derivative **10** as the major product and C–H activation/ring expansion product, **11** as minor product (Scheme 4). No aromatic C–F bond activation product was observed. Mechanistically, the initial formation of a silaoxirane derivative is

proposed, which undergoes C–C bond formation upon nucleophilic attack from the oxygen atom of another molecule of 4-fluorobenzaldehyde at the silicon center.



Scheme 4. Reaction of **7** with 4-fluorobenzaldehyde.

The preparation of **10** is highly regio- and stereospecific; the formation of the *trans* isomer was only identified. The ^{1}H NMR spectrum of **10** showed a resonance at δ 6.63 ppm which indicates the C–H protons of the C–C bond. The appearance of two new signals ^{13}C NMR spectrum at δ 114.68 and 114.89 ppm corresponds to C–C bond formation. According to the ^{19}F NMR spectrum of **10**, the C–F resonances appear at δ –118.93 and –118.99 ppm, respectively. The ^{29}Si NMR spectrum of **10** shows a resonance at δ –38.17 ppm.

Compound **10** crystallizes in the monoclinic space group $P2_1/c$ and the selected bond lengths and angles are showed in the legend of the Figure 4. The silicon atom is bound to three nitrogen atoms (two from the amidinato ligand and one from the amide substituent moiety), two oxygen atoms, and adopts a distorted trigonal bipyramidal geometry. The Si–O bond lengths are (~1.704 Å), which are slightly longer than the standard Si–O single bonds (~1.65 Å). The C22–C23 bond length is of 1.555(5) Å, comparable to the standard C–C single bond.

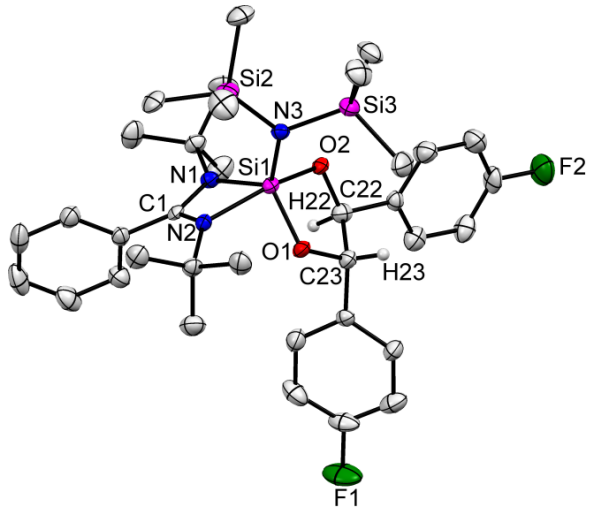


Figure 4. Molecular structure of **10**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms (except H22 and H23 are bonded to C22 and C23, respectively) are omitted for clarity. Selected bond distances (Å) and bond angles (deg): C22–C23 1.555(5), C22–H22 0.981, C23–H23 0.980, Si1–O1 1.687(3), Si1–O2 1.721(3), Si1–N1 1.821(3), Si1–N2 1.977(3), Si1–N3 1.735(3); O1–Si1–O2 89.8(1), N1–Si1–O1 117.3(1), N1–Si1–O2 96.6(1), N2–Si1–O1 85.2(1), N2–Si1–O2 159.4(1), N3–Si1–O1 123.0(1), N3–Si1–O2 99.4(1), N1–Si1–N2 68.5(1), N1–Si1–N3 117.2(1).

According to NMR studies, **11** is obtained only in a little amount. Despite several attempts, **11** could not be obtained in preparative reasonable amounts allowing for a full spectroscopic characterization. However, the ^{1}H NMR spectrum of **11** was showed a broad resonance at δ 4.90 ppm for N–H proton. The ^{19}F NMR of **11** was also displayed a signal at δ –118.96 ppm. Single crystals of **11** were developed in the same flask of **10** in the same condition. **11** crystallizes in the orthorhombic space group $P2_1/c$ and the selected bond lengths and angles are given in the legend of the Figure 5.

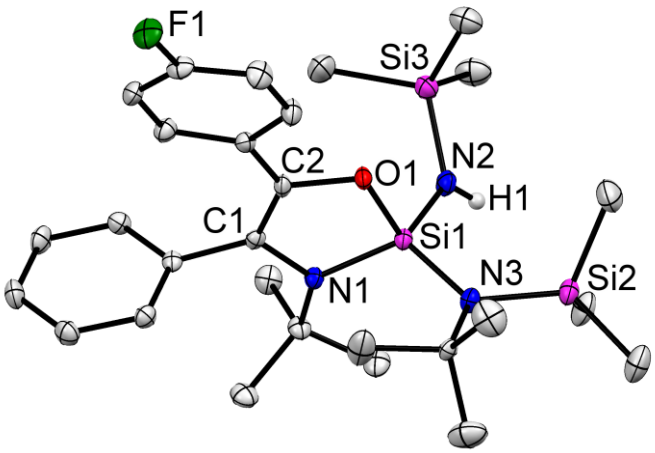
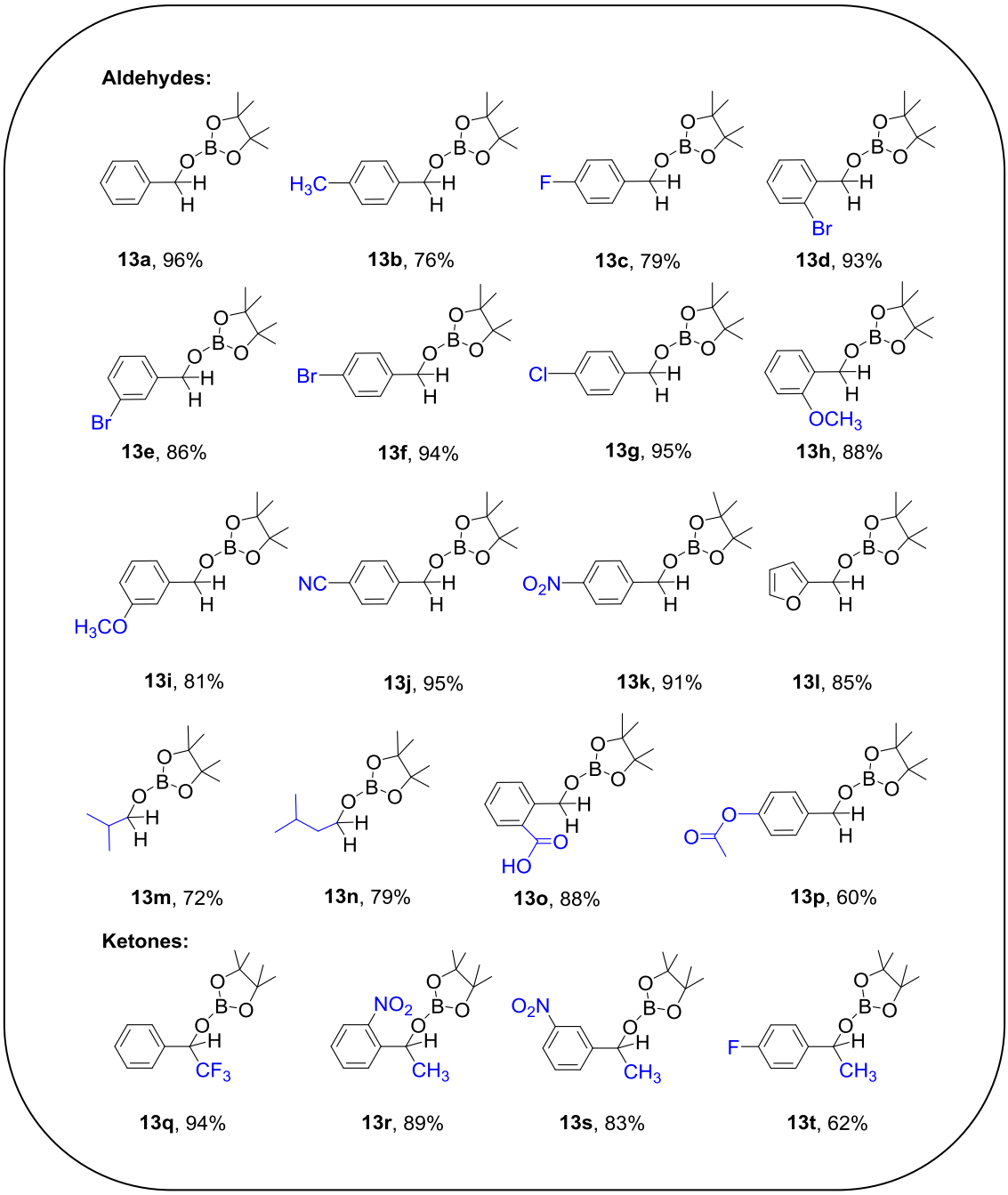


Figure 5. Molecular structure of **11**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms (except H1 is bonded to N2) are omitted for clarity. Selected bond distances (Å) and bond angles (deg): C1–C2 1.357(3), C2–O1 1.402(2), Si1–O1 1.664(1), Si1–N1 1.757(2), C1–N1 1.418(2), Si1–N2 1.700(2), Si1–N3 1.724(2), N3–Si2 1.778(2), N2–Si3 1.742(2), N3–C30 1.528(3), N2–H1 0.760(2); O1–Si1–N1 93.17(7), C1–N1–Si1 108.0(1), N1–Si1–N2 113.95(8), N1–Si1–N3 118.38(8), O1–Si1–N2 105.62(5), O1–Si1–N3 113.65(7), C2–O1–Si1 111.60(1), C1–C2–O1 113.50(2), N1–C1–C2 113.60(2), Si1–N2–H1 119.0(2), Si1–N3–Si2 119.08(9).

The silicon atom is coordinated to three nitrogen atoms, one oxygen atom, and exhibits an approximate distorted tetrahedral geometry. The Si–O bond lengths are (~1.664 Å), which are marginally longer than the standard Si–O single bonds (~1.65 Å). The C1–C2 bond length is of 1.357 (3) Å, comparable to the C=C double bond.

5.5. Application in Hydroboration of Aldehydes and Ketones

Very recently, we have demonstrated the amidinato stabilized Si (IV) compound as a single site catalyst for the hydroboration and cyanosilylation of a variety of aldehydes and ketones at ambient conditions.[19]

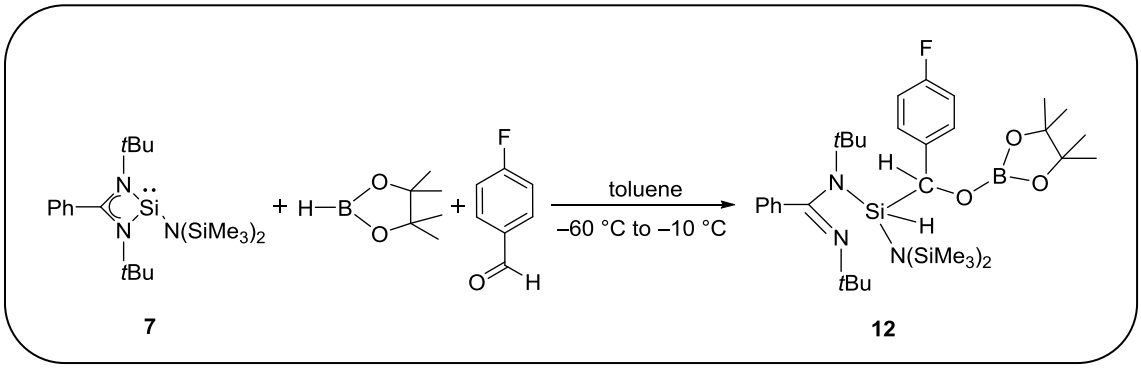


Scheme 5. Silicon (II) catalyzed hydroboration of aldehydes and ketones**.**

In contrast, Si(II) compounds have remained little used in catalysis. Inspired by this facile activation of both C=O and B–H bond, we studied the possibility of hydroboration with silylene, **7** as single site catalyst. **7** (1-2 mol %), HBpin (1.0 equiv.), and benzaldehyde (1.0 equiv.) were mixed in benzene at room temperature (entry **13a**). Consequently, the oragnoboronate esters were obtained in moderate to high yields and are presented in Scheme 5. [9c]As per our catalysis studies, the hydroboration reaction yields 25% product, without the using catalyst. Aldehydes with electron withdrawing substituents afforded higher yields (**13j**, **13k**) than electron donating substituted aromatic aldehydes (**13b**, **13h**, and **13i**). Halogenated benzaldehydes afforded the corresponding organoboronate products in excellent yields (**13c**-**13g**). Hydroboration of furan smoothly occurs at the C=O functionality to afford the respective product (**13l**). The catalyst is highly chemoselective towards the aldehyde functionality in the presence of acid and ester functional groups (**13o** and **13p**). The aliphatic aldehydes such as isobutyraldehyde and isovaleraldhyde gave the corresponding organoboronate esters at room temperature within 30 min (**13m** and **13n**). We have also investigated the hydroboration of ketones using **7** as a catalyst, but only activated ketone substrates (**13q**-**13t**) could be effectively reduced (standard conditions: 1-2 mol %, 6 h, rt).

5.6. Mechanistic Investigations

To insight into the reaction mechanism of hydroboration of carbonyl compounds with catalytic usage of silylene, we have performed a stoichiometric reaction among silylene, pinacolborane, and 4-fluorobenzaldehyde for 1h at −60 °C, afforded an unusual neutral Si(IV) derivative, **12** (Scheme 6).



Scheme 6. Formation of Si(IV) compound **12**.

Compound **12** crystallizes in the orthorhombic space group *P*bca and the selected bond lengths and angles are given in the legend of the Figure 6. The silicon atom is

coordinated to two nitrogen atoms (one from the amidinato ligand and other from the amide substituent moiety), one hydrogen atom, and one carbon atom (carbonyl carbon of 4-fluorobenzaldehyde). The silicon atom exhibits an approximate distorted tetrahedral geometry. The most unusual feature of **12** is that the silicon atom is not bound to the oxygen atom of the HBPin despite its oxophilic nature. The Si–N bond lengths are ~1.736 Å, which are comparable with the other Si–N bond lengths (1.743(3) and 1.742(3) Å). However, one of the Si–N bonds from the ligand fragment was seen to be opened.[30a] Evidence for this behaviour comes from the Si(1)–N(1) interatomic separation (3.012 Å) in **12**, which conclusively indicates that there is a weak interaction between Si1 and N1.

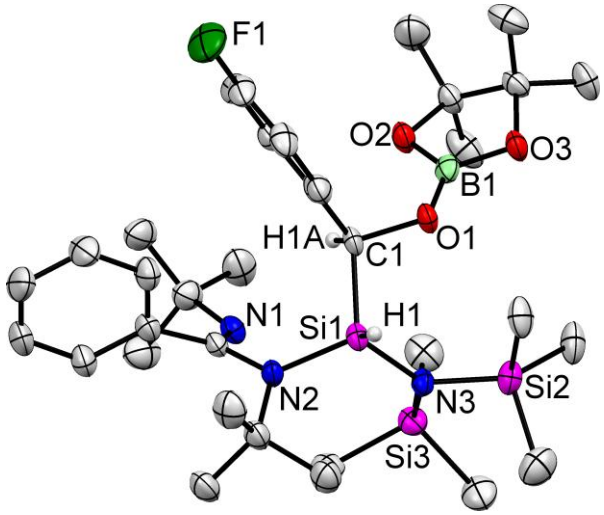


Figure 6. Molecular structure of **12**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms (except H1 and H1A are bonded to Si1 and C1, respectively) are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Si1–N2 1.744(3), Si1–N3 1.729(4), C1–Si1 1.90(4), C1–O1 1.470(4), O1–B1 1.343(6), Si1–H1 0.979, C1–H1A 0.979, N2–C8 1.431(5), N1–C8 1.270(5); N2–Si1–C1 110.8(2), N3–Si1–C1 110.3(2), Si1–C1–O1 104.6(2), Si1–C1–C2 117.3(3), C1–O1–B1 119.8(3), N1–C8–N2 115.6(3), H1–Si1–C1 104.9(0), H1A–C1–Si1 108.8(0), H1–Si1–N2 105.0(0), H1–Si1–N3 104.90(0), H1A–C1–O1 108.90(0), H1A–C1–C2 108.80(0).

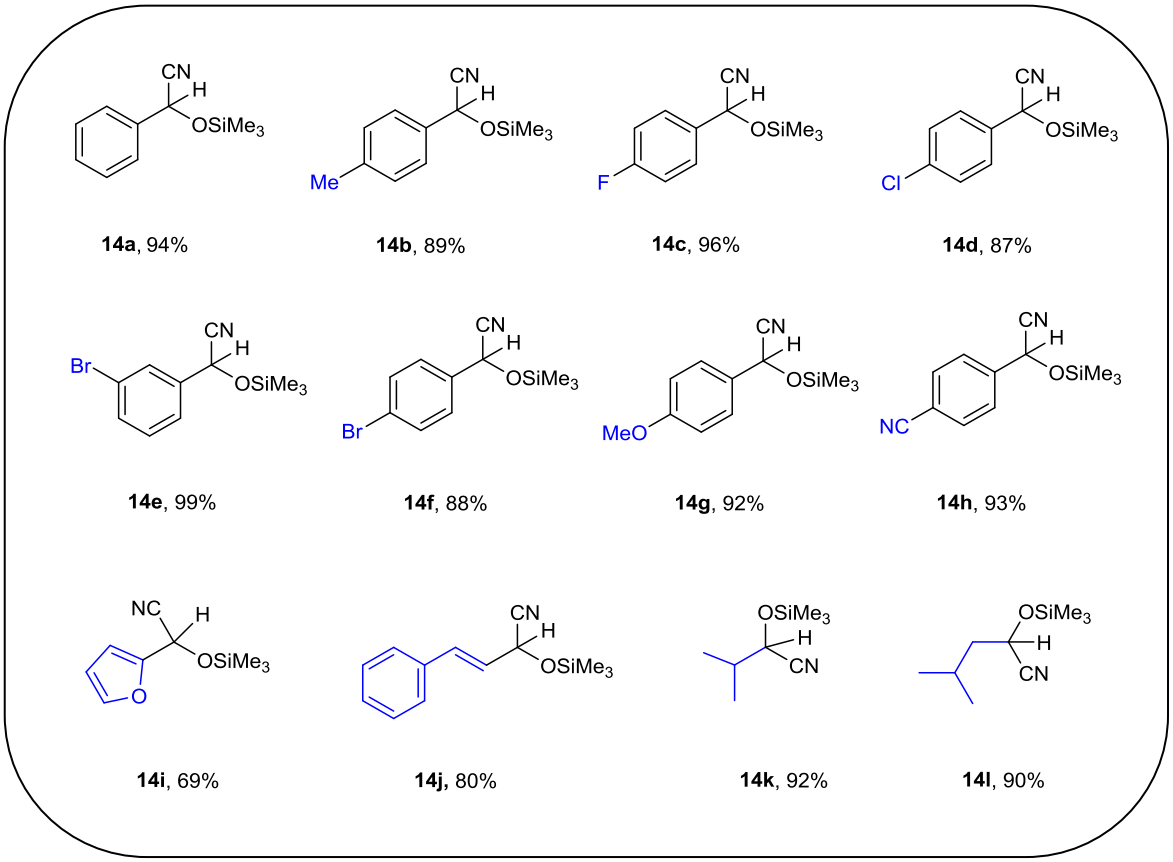
The Si–C bond is 1.90(8) Å in length, which is slightly longer than the Si–C single bonds (~1.85 Å).[19b] The longer Si–C bond length indicates that the rupture of this bond may be facile upon heating which is further confirmed by our NMR spectroscopic studies. The Si1–H1 bond length is of 0.979(4) Å, which is longer than the previously reported LSiCl(H)N(H)-

N=CPh$_2$ [L=PhC(N*t*Bu)$_2$] [1.350 Å].[32] Furthermore, the C1–H1A bond length is 0.979 is in good agreement with the compound **9** of C–H bond length (~0.981 Å).

New resonances are detected at δ 5.36 and δ 5.57 ppm in the ^{1}H NMR spectrum recorded for C–H and Si–H protons, respectively. The appearance of a sharp singlet for the amido substuent moiety in the ^{1}H NMR at δ 0.64 ppm shows that they are chemically equivalent. We also performed both ^{13}C and DEPT-135 NMRs, which show the single resonances for the methine group of (Ph*C*H(Si)O) moiety at δ 69.98 ppm and 69.66 ppm, respectively. The ^{29}Si NMR of **12** exhibits two new signals at δ –10.90 and 12.79 ppm, reflecting the four coordination of the silicon. The ^{19}F NMR shows a signal at δ -115.47 ppm corresponding to the C–F bond. Furthermore, another new resonance appears in the ^{11}B NMR at δ 20.55 ppm, indicating that three coordination of the boron atom. The molecular ion peak was observed at *m/z* 672.40 with the highest relative intensity.

5.7. Application in Cyanosilylation of Aldehydes

We further extended the catalytic activity of **7** to the cyanosilylation of aldehydes. The recent advancements with *p*-block elements employed as single site catalysts for cyanosilylation aldehydes and ketones have been reported.[19b-c,20d,33]



14a, 94% **14b**, 89% **14c**, 96% **14d**, 87%

14e, 99% **14f**, 88% **14g**, 92% **14h**, 93%

14i, 69% **14j,** 80% **14k**, 92% **14l**, 90%

Scheme 7. Silicon (II) catalyzed cyanosilylation of aldehydes.

The Scheme 7 displays the results of cyanosilylation experiments with a variety of aldehydes under optimal conditions of 2 mol% catalyst at room temperature with a 3 h reaction time.

7 is more efficient than our previously reported penta-coordinate Si(IV) catalyst for aldehyde cyanosilylation, which took 6 h for the productive catalysis.[9c] This reaction does not proceed without catalyst. The cyanosilylation reaction with benzaldehyde afforded **14a** in high yield under same optimal conditions. We have also investigated the substrate scope with a variety of aromatic and aliphatic aldehydes, which gave the corresponding cyanosilylated products in moderate to excellent yields. The electron donating as well as withdrawing substituted aromatic aldehydes furnished the corresponding cyanosilylated products (**14b**, **14g**, **14h**) in good yields. The halogenated aldehydes were exclusively cyanolsilylated at carbonyl functionality without any halogen exchange reactions with TMSCN (**14c**-**14f**). Furan clearly undergoes cyanosilylation at carbonyl functionality without affecting the heterocycle (**14i**).The cyanosilylation of cinnamaldehyde took place exclusively at the 1, 2-position leaving the olefinic functionality intact (**14j**). The aliphatic aldehydes also gave the corresponding cyanosilylated products (**14k** and **14l**) in good yields.

5.8. Conclusions

After more than 150 years since the discovery of the pinacol coupling reaction by Wilhelm Rudolph Wittig,[34] we have demonstrated that silylene (**7**) can also mediate a carbon–carbon covalent bond formation between two aldehydes leading to a 1,3-dioxasilolane derivative (**10**). No C–F bond activation was detected. The analogous reaction with benzaldehyde resulted in the cleavage of the aldehyde C–H bond and subsequent amidinate ring expansion *via* insertion of the benzoyl moiety into the C–N bond. This is also the first example of an aldehyde C–H bond activation by a silylene. The formation of the two distinctly different products can be attributed to the difference in the nature of the C=O bond in benzaldehyde and 4-fluorobenzaldehyde. The addition of HBpin to **7** resulted in a 1,3 B–H addition to **7** with the ‘‘Bpin’’ fragment translocating to the silylene center and the hydride migrating to the carbon center. Subsequently, we have demonstrated the employment of **7** as a catalyst for the reductive hydroboration of a wide range of aldehydes and ketones at mild reaction conditions. Moreover, we have also observed that **7** is an efficient catalyst for selective aldehyde cyanosilylation. We believe our results will open the door for the silylene based transition metal free catalysis, which remains as one of the decisive targets for the silicon chemists.

5.9. References

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6.1: Chapter 2; Experimental Details

6.1.1. Crystal structural details of compound 9

6.1.2. Computational details of compound 9

6.2: Chapter 3; Experimental Details

6.2.1. Crystal structural details of compounds 5, 7 and 8

6.2.2. Computational details of compound 5

6.3: Chapter 4; Experimental Details

6.3.1**.** Crystal structural details of compounds 5 and 6

6.3.2. Solvent screening for catalytic cyanosilylation of aldehydes

6.3.3. General procedure for catalytic cyanosilylation of aldehydes

6.3.4. Spectroscopic data for cyanosilylation of aldehydes

6.4: Chapter 5; Experimental Details

6.4.1**.** Crystal structural details of compounds 8 to 12

6.4.2. Solvent screening for catalytic hydroboration of aldehydes

6.4.3. General procedure for catalytic hydroboration of aldehydes

6.4.4. Spectroscopic data for hydroborated prodcuts of aldehydes

6.4.5. General procedure for catalytic hydroboration of ketones

6.4.6. Spectroscopic data for hydroborated products of ketones

6.4.7. General procedure for catalytic cyanosilylation of aldehydes

6.4.8. Spectroscopic data for cyanosilylated products of aldehydes

6.4.9. Details of DFT computations

6.1. Chapter 2; Experimental Details

6.1.1. Crystal structural details of compound 9

Crystal data 9: C_{36} H_{36} Cl_6 Ge_3 N_4, M = 956.16, yellow color, 0.34 x 0.22 x 0.17 mm^3, monoclinic, space group $P2_1/c$, a = 9.4793(10) Å, b = 16.9178(19) Å, c = 25.305(3) Å, β = 92.288(3) °, V = 4054.9(8) $Å^3$, Z = 4, T = 150(2) K, $2\theta_{max}$ = 50.498°, D_{calc} (g cm^{-3}) = 1.566, $F(000)$ = 1916, μ (mm^{-1}) = 2.636, 158406 reflections collected, 7348 unique reflections (R_{int}= 0.0621), 5586 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.776, T_{max} = 0.768, 450 refined parameters, S = 1.041, $R1$ = 0.0612, $wR2$ = 0.1731 (all data R = 0.0877, $wR2$ = 0.1965), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 4.907, $\Delta\rho_{min}$ = -0.621 ($eÅ^{-3}$).

6.1.2. Computational details of compound 9

All the calculations in this study have been performed with density functional theory (DFT), with the aid of the Turbomole 6.4 suite of programs, employing the PBE functional and the TZVP[3] basis set. The resolution of identity (RI), along with the multipole accelerated resolution of identity (marij) approximations have been used for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. Solvent correction were incorporated with optimization calculations using the COSMO model, with toluene (ε = 2.38) as the solvent. Full frequency calculations on the optimized minima and also normal mode analysis was performed for compound **9** using the same level of theory. Consequently, all reported energy values represent gas phase data at 298.15 K temperature.

The nature of germanium-carbon interaction in compound **9** was investigated with the natural bond orbitals (NBO) analysis procedures as implemented in the Gaussian 09 program. The analyses was performed at the PBEPBE/TZVP optimized geometry using the PBEPBE density functional together with the all electron TZVP basis set.

In order to gain insight into the interaction of the isocyanide ligands with the central germaniumatom, the intermolecular charge transfer in the complex has been analysed with the natural bond orbital (NBO) analysis. The energetic estimate of donor (i) – acceptor (j) orbital interactions can be obtained by the second order perturbation theory analysis of the Fock matrix in the NBO basis. The donor–acceptor interaction energy E(2) is given by

$$E(2) = \Delta E(i,j) = q(i,j)F(i,j)^2/\{\varepsilon(i) - \varepsilon(j)\}$$

where q(i) is the donor orbital occupancy, ε(i) and ε(j) are the diagonal elements (orbital energies), and F(i,j) is the off-diagonal NBO Fock matrix element. In the present

investigation, the important interactions between the cental germanium and the isocyanide ligands have been analyzed.

6.2. Chapter 3; Experimental Details

6.2.1. Crystal structural details of compounds 5, 7 and 8

Crystal data 5: $C_{29}H_{46}F_3N_3OSi_3$, M = 593.96, colorless, 0.34 x 0.23 x 0.17 mm^3, orthorhombic, space group $P2_12_12_1$, a = 10.152 (3) Å, b = 10.449 (3) Å, c = 30.517 (9) Å, $\alpha=\beta=\gamma$ = 90°, V = 3237.0 (17) $Å^3$, Z = 4, T = 296(2) K, $2\theta_{max}$ = 49.998°, D_{calc} (g cm^{-3}) = 1.219, $F(000)$ = 1272.0, μ (mm^{-1}) = 0.190, 46723 reflections collected, 5699 unique reflections (R_{int}= 0.1008), 4860 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.949, T_{max} = 0.968, 365, flack parameter x = 0.44(6), refined parameters, S = 1.162 , $R1$ = 0.0753, $wR2$ = 0.1793 (all data R = 0.0920, $wR2$ = 0.1793), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.475, $\Delta\rho_{min}$ = -0.397 ($eÅ^{-3}$).

Crystal data 7: $C_{27}H_{41}F_6N_3Si_3$, M = 605.90, colorless, 0.38x 0.28 x 0.17 mm^3, monoclinic, space group $P2_1/c$, a = 14.962 (3) Å, b = 12.796 (3) Å, c = 17.935 (4) Å, $\alpha=\gamma$= 90°, β = 113.789 (5) °, V = 3141.9 (12) $Å^3$, Z = 4, T = 296(2) K, $2\theta_{max}$ = 49.996°, D_{calc} (g cm^{-3}) = 1.281, $F(000)$ = 1280.0, μ (mm^{-1}) = 0.208, 68453 reflections collected, 5530 unique reflections (R_{int} = 0.1653), 3387 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.932, T_{max} = 0.965, 365 refined parameters, S = 1.020, $R1$ = 0.0499, $wR2$ = 0.1152 (all data R = 0.1127, $wR2$ = 0.1152), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.318, $\Delta\rho_{min}$ = -0.305 ($eÅ^{-3}$).

Crystal data 8: $C_{28}H_{41}F_8N_3Si_3$, M =655.91, colorless, 0.38 x 0.27 x 0.22 mm^3, triclinic, space group P^{-1}, a = 9.658 (2) Å, b = 9.771 (2) Å, c = 17.351 (4) Å, α = 99.448 (6) °, β = 91.554 (6) °,γ = 94.467 (6) °, V = 1609.0 (7) $Å^3$, Z = 2, T = 296(2) K, $2\theta_{max}$ = 49.998°, D_{calc} (g cm^{-3}) = 1.354, $F(000)$ = 688.0, μ (mm^{-1}) = 0.217, 45397 reflections collected, 5670 unique reflections (R_{int} = 0.1746), 3256 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.932, T_{max} = 0.953, 392 refined parameters, S = 1.038, $R1$ = 0.0713, $wR2$ = 0.1957 (all data R = 0.1457, $wR2$ = 0.1957), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.429, $\Delta\rho_{min}$ = -0.539 ($eÅ^{-3}$).

6.2.2. Computational details of compound 5

All the calculations in this study have been performed with density functional theory (DFT), with the aid of the Turbomole 7.1 suite of programs, using the PBE functional. The TZVP basis set has been employed. The resolution of identity (RI), along with the multipole accelerated resolution of identity (marij) approximations have been employed for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. Solvent correction were incorporated with optimization calculations using the COSMO model, with toluene (ε = 2.374) as the solvent. The values reported are ΔG values, with zero point energy corrections, internal energy and entropic contributions included through frequency calculations on the optimized minima with the temperature taken to be 298.15 K. Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima or transition state structures.

6.3: Chapter 4; Experimental Details

6.3.1. Crystal structural details of compounds 5 and 6

Crystal data 5: $C_{16}H_{27}Cl_1Si_1N_2$, M = 310.93, colorless, 0.34 x 0.22 x 0.17 mm^3, orthorhombic, space group $P2_1$, a = 9.4858 (18) Å, b = 11.987 (3) Å, c = 15.459 (4) Å, $\alpha=\beta=\gamma$ 90 °, V = 1757.8 (6) $Å^3$, Z = 4, T = 296(2) K, $2\theta_{max}$ = 49.998°, D_{calc} (g cm^{-3}) = 1.175, $F(000)$ = 672.0, μ (mm^{-1}) = 0.279, 50112 reflections collected, 3099 unique reflections (R_{int} = 0.0918), 2891 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.929, T_{max} = 0.954, 193 refined parameters, S = 1.151, $R1$ = 0.0646, $wR2$ = 0.1896 (all data R = 0.0703, $wR2$ = 0.1896), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 1.366, $\Delta\rho_{min}$ = -0.464 ($eÅ^{-3}$).

Crystal data 6: $C_{17}H_{27}Si_1N_3$, M = 301.5, colorless, 0.32 x 0.28 x 0.22 mm^3, orthorhombic, space group $P2_1$, a = 9.527 (3) Å, b = 12.162 (3) Å, c = 15.346 (4) Å, $\alpha=\beta=\gamma$ 90 °, V = 1778.1 (10) $Å^3$, Z = 4, T = 296 (2) K, $2\theta_{max}$=49.992°, D_{calc} (g cm^{-3}) = 1.126, $F(000)$ = 656.0, μ (mm^{-1}) = 0.131, 48296 reflections collected, 3132 unique reflections (R_{int}=0.3217), 1718 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.959, T_{max} = 0.972, 202 refined parameters, S = 1.009, $R1$ = 0.0668, $wR2$ = 0.1514 (all data R = 0.1731, $wR2$ =0.1514), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.268, $\Delta\rho_{min}$= -0.260 ($eÅ^{-3}$).

6.3.2. Solvent screening for catalytic cyanosilylation of aldehydes

However, we actually tried with various solvents. Finally, we concluded that benzene is a better non-polar solvent for this after careful analysis of conversions by ^{1}H NMR spectroscopy. The solvent entry is shown below.

S. NO.	R	Solvent	Catalyst in mol%	Time (h)	Conversion (%)
1.	H	Benzene	3	1	80
2.	H	DCE	3	1	70
3.	H	Hexane	3	1	53
4.	H	DCM	3	1	36
5.	H	Toluene	3	1	>90

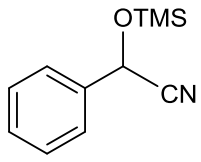
6.3.3. General procedure for catalytic cyanosilylation of aldehydes

To a benzene solution of aldehyde (1 mmol), TMSCN (1 mmol) and compound **5** (3 mol%) were stirred under argon atmosphere for 6 h at ambient conditions. After finish the desired time, the reaction mixture was filtered followed by removal of solvent under reduced pressure. The crude was dissolved in $CDCl_3$ and analysed by ^{1}H and ^{13}C NMR spectroscopy.

6.3.4. Spectroscopic data for cyanosilylation of aldehydes

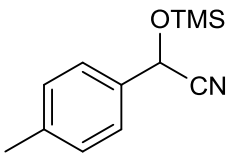
The spectroscopic data of compound **7a** and **7b** (NMR studies with benzaldehyde) is similar to compound 7c. The spectra of compounds **7c**-**7s** indicate the reaction of aldhyde with TMSCN under standard conditions.

Compound 7c:



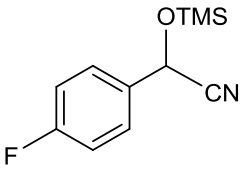
^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 7.47-7.37 (m, 5H, Ph), 5.51 (S, 1H, CH), 0.25 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 25 ^{o}C) δ 136.19, 129.25, 128.85, 128.07, 126.26 (Ph), 119.11(CN), 63.58(OCH), 30.83, 0.94, -0.35 ($SiMe_3$) ppm.

Compound 7d:



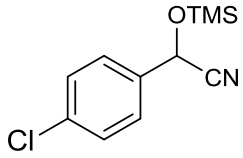
^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 7.31-7.24 (d, 2H, Ph), 7.17-7.13 (d,2H, Ph), 5.39 (S, 1H, CH), 0.15 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 25 ^{o}C) δ 129.83, 129.61, 129.57, 126.36, (Ph), 119.27 (CN), 63.54 (OCH), 21.17 (CH_3), 0.27 ($SiMe_3$) ppm.

Compound 7e:



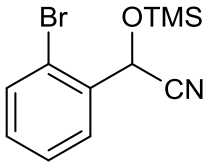
^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 7.36 (dd, 2H, Ph), 7.01 (dd, 2H, Ph) 5.39 (S, 1H, CH), 0.15 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 298 K) δ 165.57, 160.63, 132.30, 128.31, 118.95 (Ph), 116.13 (CN), 62.94 (OCH), 30.87, 1.23, -0.35 ($SiMe_3$) ppm.

Compound 7f:



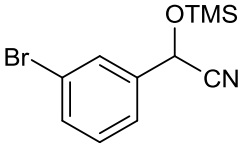
^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 7.31-7.27 (m, 4H, ArCH), 5.38 (S, 1H, CH), 0.15 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 25 ^{o}C) δ 140.95, 130.90, 129.46, 129.17, 127.67 (CN), 62.98 (OCH), 1.01 ($SiMe_3$) ppm.

Compound 7g:



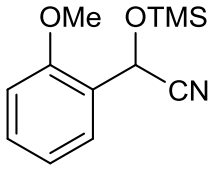
^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 7.61-7.17 (m, 4H, Ph), 5.68 (S, 1H, CH), 0.17 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 25 ^{o}C) δ 135.44, 132.95, 130.84, 128.53, 128.13, 121.66 (Ph), 118.28 (CN), 63.16 (OCH), 30.94, 0.98 ($SiMe_3$) ppm.

Compound 7h:



^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 7.54-7.17 (m, 4H, ArCH), 5.37 (S,1H, CH), 0.17 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 25 ^{o}C) δ 137.27, 132.31, 130.47, 128.30, 124.80 (Ph), 118.62 (CN), 62.81 (OCH), - 0.31 ($SiMe_3$) ppm.

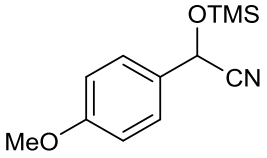
Compound 7i:



^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 7.62 (dd, 1H, Ph), 7.37 (td, 1H, Ph), 7.08-6.89 (m, 2H, Ph), 5.81 (S, 1H, CH), 3.89 (S, 3H, OCH_3), 0.24 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 25 ^{o}C) δ 134.98, 133.95, 128.71, 126.93, 123.49, 122.82 (Ph), 118.35 (CN), 62.20 (OCH), 61.58 (OCH_3), 30.87, 0.97, -0.16 ($SiMe_3$) ppm.

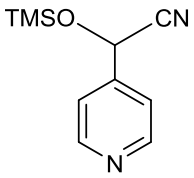
Compound 7j:

^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 7.42-7.38(d, 2H, Ph), 6.95-6.91 (d,2H, Ph), 5.45 (S, 1H, CH), 3.83(S, 3H, OCH_3), 0.22 (S, 9H,



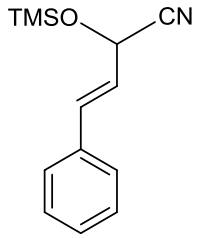
$SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 25 ^oC) δ 134.98, 133.95, 128.71, 126.93, 123.49, 122.82 (Ph), 118.35 (CN), 62.20 (OCH), 61.58 (OCH_3), 30.87, 0.97, -0.16 ($SiMe_3$) ppm.

Compound 7k:



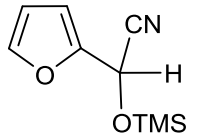
^1H NMR (200 MHz, $CDCl_3$, 298 K) δ 8.66-8.63 (d, 2H, ArCH),7.42-7.39 (d,1H, ArCH), 5.51 (S, 1H, CH), 0.27 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 25 ^oC) δ 150.80, 150.05, 148.45,122.96, 121.76 (ArC), 120.67 (CN), 62.20 (OCH), 1.87, 0.16 ($SiMe_3$) ppm

Compound 7l:



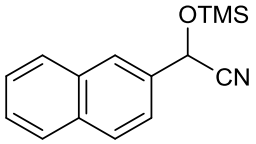
^1H NMR (200 MHz, $CDCl_3$, 298 K) δ 7.27-7.24 (m, 5H, Ph), 6.73-6.66 (d,1H, ArCH), 6.12-6.02 (d,1H, ArCH), 4.99 (S, 1H, CH), 0.14 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 25 ^oC) δ 146.8, 133.95, 128.71, 126.93, 123.49 (Ph), 118.35 (CN), 62.20 (OCH), 30.87, 0.97ppm.

Compound 7m:



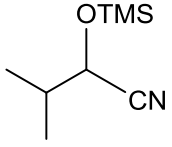
^1H NMR (200 MHz, $CDCl_3$, 298 K) δ 7.37-7.36 (q, 1H, ArCH), 6.46-6.44 (d,1H, ArCH), 6.33-6.30 (d, 1H, ArCH), 5.45 (S, 1H, CH), 0.11 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 25 ^oC) δ148.06, 128.29, 117.12, 110.80,109.73 (CN), 57.44 (OCH), 0.98, -0.40 ($SiMe_3$) ppm.

Compound 7n:



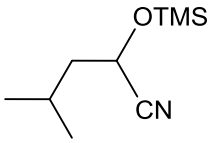
^1H NMR (200 MHz, $CDCl_3$, 298 K) δ 8.23-7.39 (m, 7H, Ph), 6.08 (S, 1H, CH), 0.23 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 25 ^oC) δ 136.66, 135.23, 133.25, 133.90, 130.39, 128.90, 126.93, 126.24, 125.39, 125.02, 123.10 (Ph), 119.05 (CN), 62.65(OCH), 30.88, 0.98, -0.23($SiMe_3$) ppm.

Compound 7o:



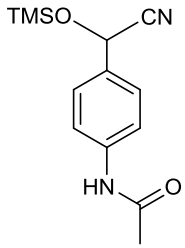
^1H NMR (200 MHz, $CDCl_3$, 298 K) δ 4.16-4.13 (d, 1H, CH), 1.92 (sept,1H, $CH(CH_3)_2$), 1.01 (S, 6H, $CH(CH_3)_2$), 0.18 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 25 ^oC) δ 119.16 (CN), 67.12 (OCH), 33.73 ($CH(CH_3)_2$), 17.44, 17.11 ($CH(CH_3)_2$), 0.60 ($SiMe_3$) ppm.

Compound 7p:



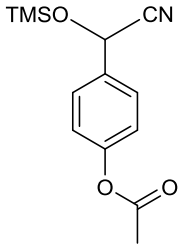
^{1}H NMR (200 MHz, $CDCl_3$, 298 K) δ 4.42 (t, 1H, CH), 1.80 (t,2H, CH_2), 1.66 (m, 1H, $CH(CH_3)_2$), 0.96-0.91 (d, 6H, $CH(CH_3)_2$), 0.20 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 298 K) δ 120.22 (CN), 59.85 (OCH), 44.84 ($CH(CH_3)_2$), 24.0, 22.44, 21.82 ($CH(CH_3)_2$), - 0.47 ($SiMe_3$) ppm.

Compound 7q:



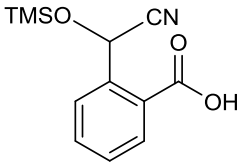
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 8.02 (b, 1H, NH), 7.58 (d, 2H, Ph), 7.40 (d, 2H, Ph), 5.46 (S, 1H, CH), 2.17 (S, 3H, CH_3), 0.21 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 25 ^{o}C) δ 168.84 ($NH(CO)CH_3$), 139.09, 131.74, 131.06, 127.11, 120.04 (Ph), 119.24 (CN), 63.27 (OCH), 24.45 (CH_3), 0.96 ($SiMe_3$) ppm.

Compound 7r:



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.36 (d, 2H, Ph), 7.23 (d, 2H, Ph), 5.57 (S, 1H, CH), 2.38 (S, 3H, CH_3), 0.32 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 25 ^{o}C) δ 168.85 ($Ph(COO)CH_3$), 151.26, 133.76, 131.17, 127.50, 122.33 (Ph), 118.94 (CN), 63.02 (OCH), 21.06 (CH_3), 0.96, -0.32 ($SiMe_3$) ppm.

Compound 7s:



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 10.68 (b, 0.1H, COOH), 7.66-7.53 (m, 4H, Ph), 6.59 (S, 1H, CH), 0.21 (S, 9H, $SiMe_3$) ppm; ^{13}C NMR (50.28 MHz, $CDCl_3$, 25 ^{o}C) δ 168.75 (Ph(COOH)), 147.59, 134.38, 130.41, 128.15, 126.63, 125.33, (Ph), 122.97 (CN), 97.45 (OCH), 0.96, 0.14 ($SiMe_3$) ppm.

6.4: Chapter 5; Experimental Details

6.4.1. Crystal structural details of compounds 8 to 12

Crystal data 8: $C_{27}H_{54}B_1N_3O_2Si_3$, M = 547.81, colorless, 0.33 x 0.25 x 0.16 mm^3, orthorhombic, space group *P* bca, *a* = 11.4586 (16) Å, *b* = 19.143 (3) Å, *c* = 30.168 (4) Å, $\alpha=\beta=\gamma$ =90°, *V* = 6617.4 (16) Å^3, *Z* = 8, *T* = 296(2) K, $2\theta_{max}$=124.998°, D_{calc} (g cm^{-3}) = 1.100, *F*(*000*) = 2400, μ (mm^{-1}) = 1.516, 124812 reflections collected, 5261 unique reflections (R_{int}= 0.1669), 4011 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption

correction, T_{min} = 0.666, T_{max} = 0.785, 346 refined parameters, *S* = 1.198, *R*1 = 0.0742, *wR*2 = 0.2282 (all data *R* = 0.1006, *wR*2 =0.2282), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.544, $\Delta\rho_{min}$= -0.830 (eÅ^{-3}).

Crystal data 9: $C_{28}H_{47}N_3O_1Si_3$, M =525.95, colorless, 0.38 x 0.28 x 0.18 mm^3, triclinic, space group *P* -1, *a* = 10.8132 (14) Å, *b* = 10.9099 (13) Å, *c* = 13.5038 (17) Å, α = 80.743 (3) °, β = 78.036 (3) °, γ = 79.717 (3) °, *V* = 5120.7 (3) Å^3, *Z* = 2, *T* = 296 (2) K, $2\theta_{max}$=49.994°, D_{calc} (g cm^{-3}) = 1.149, *F*(*000*) = 572.0, μ (mm^{-1}) = 0.181, 54149 reflections collected, 5343 unique reflections (R_{int}= 0.1319), 3489 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.941, T_{max} = 0.968, 329 refined parameters, *S* = 1.026, *R*1 = 0.0535, *wR*2 = 0.1049 (all data *R* = 0.1084, *wR*2 =0.1049), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.301, $\Delta\rho_{min}$= -0.403 (eÅ^{-3}).

Crystal data 10:$C_{35}H_{51}F_2N_3O_2Si_3$, M =668.05, colorless, 0.38 x 0.28 x 0.17 mm^3, monoclinic, space group *P* 2_1/c, *a* = 11.174 (4) Å, *b* = 16.174 (6) Å, *c* = 20.535 (8) Å, α= γ = 90°, β =101°.522 (9), *V* = 3636 (2) Å^3, *Z* = 4, *T* = 296(2) K, $2\theta_{max}$=50.00°, D_{calc} (g cm^{-3}) = 1.220, *F*(*000*) = 1432, μ (mm^{-1}) = 0.175, 123259 reflections collected, 6408 unique reflections (R_{int}= 0.2604), 3736 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.943, T_{max} = 0.971, 419 refined parameters, *S* = 1.046, *R*1 = 0.0693, *wR*2 = 0.1185 (all data *R* = 0.1479, *wR*2 = 0.1185), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.353, $\Delta\rho_{min}$= -0.285 (eÅ^{-3}).

Crystal data 11. $C_{28}H_{46}F_1N_3O_1Si_3$, M = 543.95, colorless, 0.38 x 0.28 x 0.17 mm^3, orthorhombic, space group *P* 2_1/c, *a* = 11.5454 (3) Å, *b* = 16.4615 (4) Å, *c* = 17.4112 (4) Å, α = γ = 90 °, β = 106.504 (10) °, *V* = 3172.5 (14) Å^3, *Z* = 4, *T* = 217 (2) K, $2\theta_{max}$ = 49.99°, D_{calc} (g cm^{-3}) = 1.139, *F*(*000*) = 1176.0, μ (mm^{-1}) = 0.179, 28441 reflections collected, 5477 unique reflections (R_{int}= 0.0294), 4667 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.924, T_{max} = 0.965, 341 refined parameters, *S* = 1.020, *R*1 = 0.0377, *wR*2 = 0.0923 (all data *R* = 0.0469, *wR*2 = 0.0923), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.368, $\Delta\rho_{min}$ = -0.329 (eÅ^{-3}).

Crystal data 12. $C_{34}H_{59}B_1F_1N_3O_3Si_3$, M = 671.92, colorless, 0.38 x 0.28 x 0.18 mm^3, orthorhombic, space group *P* bca, *a* = 12.478 (6) Å, *b* = 19.001 (9) Å, *c* = 33.150 (16) Å, α =β = γ = 90 °, *V* = 7860 (7) Å^3, *Z* = 8, *T* = 293 (2) K, $2\theta_{max}$ = 49.99°, D_{calc} (g cm^{-3}) = 1.136, *F*(*000*) = 2912.0, μ (mm^{-1}) = 0.160, 261136 reflections collected, 6913 unique reflections

(R_{int}= 0.4083), 4001 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.941, T_{max} = 0.972, 423 refined parameters, S = 1.039, $R1$ = 0.0722, $wR2$ = 0.1757 (all data R = 0.1461, $wR2$ =0.1757), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.369, $\Delta\rho_{min}$= -0.303 (eÅ^{-3}).

6.4.2. Solvent screening for catalytic hydroboration of aldehydes

Aldehyde (0.25 mmol), pinacolborane (0.25 mmol) and **7** (1-2 mol%) were performed in a Schlenk tube, in various polar and non polar solvents. According to the stability of catalyst and NMR yield of the various solvents, we finally chose benzene/toluene as a suitable non-polar solvent to perform all the catalytic reactions under mild reaction conditions. The solvent entry is shown below.

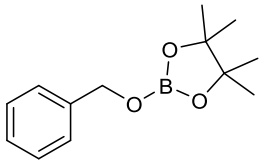
S. NO.	R	Solvent	Catalyst in mol%	Time (h)	Conversion (%)
1.	H	Benzene	2	1.5	>90
2.	H	Toluene	2	1.5	89
3.	H	Hexane	2	2	77
4.	H	DCM	2	2	85
5.	H	THF	2	2	81

6.4.3. General procedure for catalytic hydroboration of aldehydes

Aldehyde (0.25 mmol), pinacolborane (0.25 mmol) and [PhC(N*t*Bu)$_2$SiN(SiMe$_3$)$_2$] (1-2 mol%) [benzene (2 mL)] were charged in Schlenk tube inside glove box. The reaction mixture was allowed to run at room temperature for 2 h reaction time. The progress of the reaction was monitored by ^{1}H and ^{13}C NMR, which indicated the completion of the reaction by the disappearance of the aldehyde proton and appearance of a new CH_2/CH peak. Upon completion of reaction the solvent was removed using high vacuum in Schlenk line and mesitylene (0.25 mmol) as an internal standard, was added while making the NMR in $CDCl_3$.

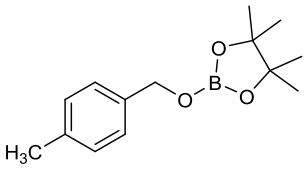
6.4.4. Spectroscopic data for hydroborated prodcuts of aldehydes

2-(benzyloxy)-pinacolborane (**13a**):



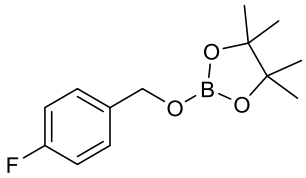
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.18 (s, 12H, CH_3), 4.86 (s, 2H, CH_2), 7.28-7.18 (m, 5H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.49 (*C*H_3), 66.58 (*C*H_2), 82.85 (*C*$(CH_3)_2$), 126.63, 126.82, 128.18, 137.56 (Ar-*C*) ppm.

2-((4-methylbenzyl)oxy)-pinacolborane (**13b**):



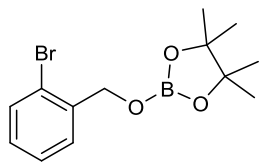
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.20 (s, 12H, CH_3), 4.82 (s, 2H, CH_2), 7.05 (d, $^{3}J_{HH}$ = 7.69 Hz, 2H, Ar*H*), 7.23 (d, $^{3}J_{HH}$ = 7.96 Hz, 2H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.54 (*C*H_3), 66.53 (*C*H_2), 82.82 (*C*$(CH_3)_2$), 128.89, 129.63, 136.2, 136.9 (Ar-*C*) ppm.

2-((4-fluorobenzyl)oxy)-pinacolborane (**13c**):



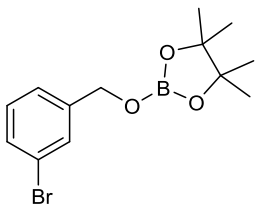
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.18 (s, 12H, CH_3), 4.80 (s, 2H, CH_2), 6.93 (d, $^{3}J_{HH}$ = 8.84 Hz, 2H, Ar*H*), 7.23 (d, $^{3}J_{HH}$ = 8.34 Hz, 2H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.52 (*C*H_3), 66.01 (*C*H_2), 83.0 (*C*$(CH_3)_2$), 115.06 (d, $J_{C\text{-}F}$ = 21.22 Hz, Ar-*C*), 128.52 (d, $J_{C\text{-}F}$ = 8.05 Hz, Ar-*C*), 132.07 (Ar-*C*), 162.18 (d, $J_{C\text{-}F}$ = 245.17 Hz, Ar*C*-F) ppm.

2-((2-bromobenzyl)oxy)-pinacolborane (**13d**):



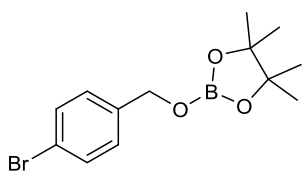
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.20 (s, 12H, CH_3), 4.90 (s, 2H, CH_2), 7.45-7.04 (m, 4H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.57 (*C*H_3), 66.25 (*C*H_2), 83.09 (*C*$(CH_3)_2$), 121.51, 127.30, 127.78, 128.56, 132.21 (Ar-*C*) ppm.

2-((3-bromobenzyl)oxy)-pinacolborane (**13e**):



^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.18 (s, 12H, CH_3), 4.80 (s, 2H, CH_2), 7.44-7.15 (m, 4H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.57 (*C*H_3), 65.79 (*C*H_2), 83.11 (*C*$(CH_3)_2$), 125.11, 128.29, 129.82, 130.39, 132.31, 141.48 (Ar-*C*) ppm.

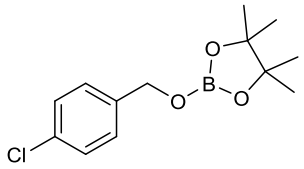
2-((4-bromobenzyl)oxy)-pinacolborane (**13f**):



^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.17 (s, 12H, CH_3), 4.78 (s, 2H, CH_2), 7.14 (d, $^{3}J_{HH}$ = 8.21 Hz, 2H, Ar*H*), 7.36 (d, $^{3}J_{HH}$ = 8.46 Hz, 2H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298

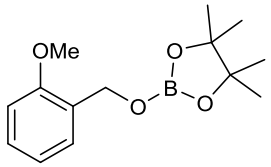
K): δ 24.52 (*C*H_3), 65.90 (*C*H_2), 83.05 (*C*$(CH_3)_2$), 121.17, 128.36, 131.32, 138.15 (Ar-*C*) ppm.

2-((4-Chlorobenzyl)oxy)-pinacolborane (**13g**):



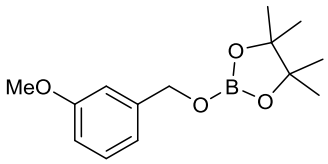
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.17 (s, 12H, C*H*$_3$), 4.80 (s, 2H, C*H*$_2$), 7.28-7.20 (m, 4H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.54 (*C*H_3), 65.90 (*C*H_2), 83.04 (*C*$(CH_3)_2$), 126.86, 128.06, 128.38, 133.08 (Ar-*C*) ppm.

2-((2-methoxybenzyl)oxy)-pinacolborane (**13h**):



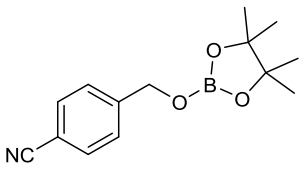
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.18 (s, 12H, C*H*$_3$), 3.71 (s, 3H, OC*H*$_3$), 4.90 (s, 2H, C*H*$_2$), 7.35-6.76 (m, 4H, Ar*H*), ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.56 (*C*H_3), 55.09 (O*C*H_3), 62.22 (*C*H_2), 82.77 (*C*$(CH_3)_2$), 109.72, 120.28 127.28, 127.66, 128.16, 128.28 (Ar-*C*), 156.44 (Ar*C*-OMe) ppm.

2-((3-methoxybenzyl)oxy)-pinacolborane (**13i**):



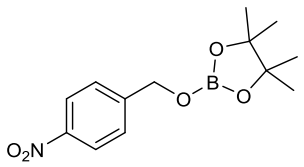
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.18 (s, 12H, C*H*$_3$), 3.71 (s, 3H, OC*H*$_3$), 4.83 (s, 2H, C*H*$_2$), 7.15-6.85 (m, 4H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.55 (*C*H_3), 55.11 (O*C*H_3), 66.51 (*C*H_2), 82.93 (*C*$(CH_3)_2$), 111.82, 113.15, 118.84, 129.25, 140.81, 159.65 (Ar-*C*) ppm.

4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzonitrile (**13j**):



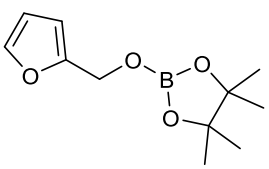
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.18 (s, 12H, C*H*$_3$), 4.89 (s, 2H, C*H*$_2$), 7.27 (d, $^3J_{HH}$ = 8.08 Hz, 2H, Ar*H*), 7.56 (d, $^3J_{HH}$ = 8.34 Hz, 2H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.50 (*C*H_3), 65.66 (*C*H_2), 83.24 (*C*$(CH_3)_2$), 111.01 (Ar*C*N) 118.76, 128.23, 132.07, 144.49 (Ar-*C*) ppm.

2-((4-nitrobenzyl)oxy)-pinacolborane (**13k**):



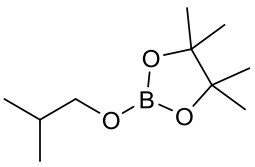
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.19 (s, 12H, C*H*$_3$), 4.94 (s, 2H, C*H*$_2$), 7.43 (d, $^3J_{HH}$ = 8.84 Hz, 2H, Ar*H*), 8.12 (d, $^3J_{HH}$ = 8.84 Hz, 2H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.55 (*C*H_3), 65.50 (*C*H_2), 83.55 (*C*$(CH_3)_2$), 123.54, 126.80 128.28, 146.54 (Ar-*C*) ppm.

2-(furfuryloxy)-pinacolborane (**13l**):



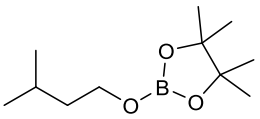
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.33 (s, 12H, CH_3), 4.89 (s, 2H, CH_2), 6.86 (s, 2H, Ar*H*), 7.43 (s, 1H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.54 (*C*H_3), 59.15 (*C*H_2), 83.00 (*C*$(CH_3)_2$), 108.24, 110.19, 142.38, 152.43 (Ar-*C*) ppm.

2-isobutoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**13m**):



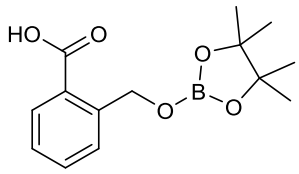
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 0.97 (d, $^{3}J_{HH}$ =6.69 Hz, 6H, CH(CH_3)$_2$), 1.30 (s, 12H, CH_3), 1.87 (sept,1H, C*H*$(CH_3)_2$), 3.69 (d, $^{3}J_{HH}$ =6.44 Hz, 2H, CH_2) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 18.65 (*C*H_3), 24.48 (*C*H_3), 29.74 (*C*H(CH_3)$_2$), 71.28 (*C*H_2), 82.46 (*C*$(CH_3)_2$) ppm.

2-valeraoxy -4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**13n**):



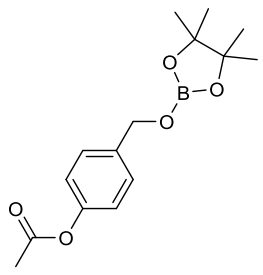
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 0.97 (d, $^{3}J_{HH}$ =6.57 Hz, 6H, CH(CH_3)$_2$), 1.53 (q, 2H, CH_2), 1.78 (sept, 1H, C*H*$(CH_3)_2$), 3.93 (t, 2H, CH_2) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 21.05 (*C*H_3), 22.40 (*C*H_3), 24.46 (*C*H), 40.23 (*C*H_2), 63.19 (*C*H_2), 82.42 (*C*$(CH_3)_2$) ppm.

2-((2-carboxybenzyl)oxy)-pinacolborane (**13o**):



^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.20 (s, 12H, CH_3), 5.32 (s, 2H, CH_2), 7.53-7.39 (m, 2H, Ar*H*), 7.66 (m, 1H, Ar*H*), 8.04 (m, 1H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.52 (*C*H_3), 65.13 (*C*H_2), 82.96 (*C*$(CH_3)_2$), 126.74, 128.26, 129.84, 131.32, 133.06, 142.51 (Ar-*C*), 171.86 (Ar*C*OOH) ppm.

2-((4-acetoxybenzyl)oxy)-pinacolborane (**13p**):



^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.18 (s, 12H, CH_3), 2.24 (s, 3H, CH_3), 4.83 (s, 2H, CH_2), 6.99 (d, $^{3}J_{HH}$ = 8.59 Hz, 2H, Ar*H*), 7.20 (d, $^{3}J_{HH}$ = 8.46 Hz, 2H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.51 (*C*H_3), 66.02 (*C*H_2), 82.96 (*C*$(CH_3)_2$), 121.32, 128.26, 131.11, 136.80, 155.28 (Ar-*C*), 169.40 (ArO(*C*O)CH_3) ppm.

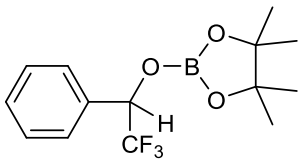
6.4.5. General procedure for catalytic hydroboration of ketones

Ketone (0.25 mmol), pinacolborane (0.25 mmol) and [PhC(N*t*Bu)$_2$SiN(SiMe$_3$)$_2$] (1-2 mol%) [benzene (2 mL)] were charged in Schlenk tube inside glove box. The reaction mixture was

allowed to run at room temperature for 6 h reaction time. The progress of the reaction was monitored by ^{1}H and ^{13}C NMR. Upon completion of reaction the solvent was removed using high vacuum in Schlenk line and mesitylene (0.25 mmol) as an internal standard, was added while making the NMR in $CDCl_3$.

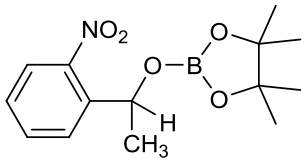
6.4.6. Spectroscopic data for hydroborated products of ketones

(Ph)(CF_3)CHOBpin (**13q**):



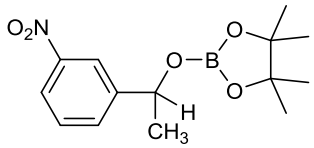
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.26 (s, 6H, CH_3), 1.30 (s, 6H, CH_3), 5.43 (q, 1H, pinBOCH), 7.41-7.51 (m, 5H, ArH) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 21.16 (CH$_3$), 73.93 (CF$_3$), 74.58 (OCHPh), 83.83 (Bpin-C), 128.28, 128.34, 129.31, 133.46, (Ar-C) ppm; ^{19}F NMR ($CDCl_3$, 376.50 MHz, 298 K): δ -78.21 (CF_3) ppm.

(2-NO_2-Ph)(CF_3)CHOBpin (**13r**):



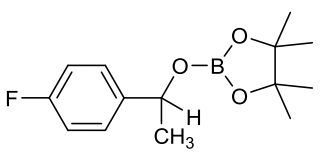
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.19 (s, 6H, CH_3), 1.24 (s, 6H, CH_3), 1.61 (d, $^{3}J_{HH}$=6.32 Hz, 3H, OCHCH_3), 5.82 (q, 1H, pinBOCH), 7.37-7.95 (m, 5H, ArH) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 21.12 (CH$_3$), 71.62 (OCHPh), 83.83 (Bpin-C), 120.53, 123.14, 131.46, 133.69, 146.53 (Ar-C) ppm.

(3-NO_2-Ph)(CF_3)CHOBpin (**13s**):



^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.26 (s, 6H, CH_3), 1.28 (s, 6H, CH_3), 1.57 (d, $^{3}J_{HH}$=6.44 Hz, 3H, OCHCH_3), 5.34 (q, 1H, pinBOCH), 7.48-7.71 (m, 2H, ArH), 8.11-8.33 (m, 2H, ArH) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 21.11 (CH$_3$), 68.19 (OCHPh), 82.98 (Bpin-C), 123.98, 127.69, 133.46, 140.46, 147.23 (Ar-C) ppm.

(4-F-Ph)(CF_3)CHOBpin (**13t**):



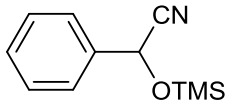
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.21 (s, 6H, CH_3), 1.26 (s, 6H, CH_3), 1.62 (d, $^{3}J_{HH}$=6.32 Hz, 3H, OCHCH_3), 5.84 (q, 1H, pinBOCH), 7.39-7.48 (m, 2H, ArH), 7.62-7.78 (m, 2H, ArH) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 21.09 (CH$_3$), 68.18 (OCHPh), 82.96 (Bpin-C), 123.91, 127.75, 128.32, 133.45, 140.43 (Ar-C) ppm.

6.4.7. General procedure for catalytic cyanosilylation of aldehydes

To a benzene solution of aldehyde (1 mmol), TMSCN (1 mmol) and [PhC(N*t*Bu)$_2$SiN(SiMe$_3$)$_2$] (2 mol%) were stirred under argon atmosphere for 3 h at ambient conditions. After finish the desired time the solvent was removed using high vacuum in Schlenk line and mesitylene (1 mmol) as an internal standard, was added while making the NMR in $CDCl_3$.

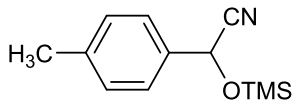
6.4.8. Spectroscopic data for cyanosilylated products of aldehydes

Compound 14a:



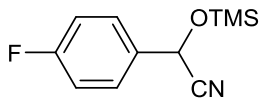
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 0.11 (s, 9H, Si*Me*$_3$), 5.37 (s, 1H, C*H*), 7.47-7.17 (m, 5H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ -0.30 (Si*Me*$_3$), 63.64 (O*C*H), 119.14 (*C*N), 126.33, 128.90, 129.30, 136.27 (Ar-*C*) ppm.

Compound 14b:



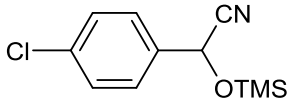
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 0.13 (s, 9H, Si*Me*$_3$), 2.28 (s, 3H, C*H*$_3$), 5.36 (s,1H, C*H*), 7.10 (d, $^3J_{HH}$ = 7.96 Hz, 2H, Ar*H*), 7.29 (d, $^3J_{HH}$ = 8.21 Hz, 2H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ -0.28 (Si*Me*$_3$), 63.54 (O*C*H), 119.26 (*C*N), 126.36, 129.55, 133.42, 139.30 (Ar-*C*) ppm.

Compound 14c:



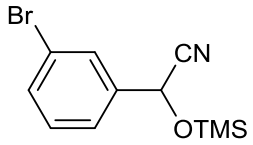
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 0.15 (s, 9H, Si*Me*$_3$), 5.37 (s,1H, C*H*), 7.00 (d, $^3J_{HH}$ = 8.72 Hz, 2H, Ar*H*), 7.37 (d, $^3J_{HH}$ = 8.84 Hz, 2H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 0.97 (Si*Me*$_3$), 62.94 (O*C*H), 115.89 (d, $J_{C\text{-}F}$= 21.96 Hz, Ar-*C*), 118.93 (CN), 128.31 (d, $J_{C\text{-}F}$ = 8.42 Hz, Ar-*C*), 132.22 (Ar-*C*), 163.11 (d, $J_{C\text{-}F}$= 248.46 Hz, Ar*C*-F) ppm.

Compound 14d:



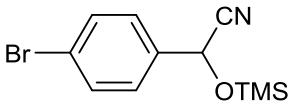
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 0.28 (s, 9H, Si*Me*$_3$), 5.50 (s, 1H, C*H*), 7.44-7.27 (m, 4H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 0.99 (Si*Me*$_3$), 62.96 (O*C*H), 118.76 (*C*N), 127.65, 129.14, 130.86, 134.84 (Ar-*C*) ppm.

Compound 14e:



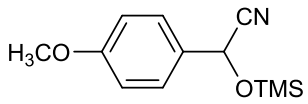
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 0.17 (s, 9H, Si*Me*$_3$), 5.36 (s,1H, C*H*), 7.54-7.19 (m, 4H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 0.98 (Si*Me*$_3$), 62.79 (O*C*H), 118.61 (*C*N), 122.93, 124.79, 126.86, 130.45, 132.44, 138.34 (Ar-*C*) ppm.

Compound 14f:



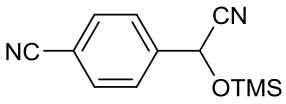
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 0.15 (s, 9H, Si*Me*$_3$), 5.35 (s,1H, C*H*), 7.43 (d, $^{3}J_{HH}$ = 8.46 Hz, 2H, Ar*H*), 7.60 (d, $^{3}J_{HH}$ = 8.21 Hz, 2H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 1.0 (Si*Me*$_3$), 63.02 (O*C*H), 118.68 (*C*N), 127.92, 130.93, 132.11, 135.35 (Ar-*C*) ppm.

Compound 14g:



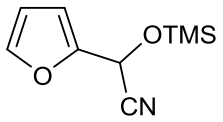
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 0.26 (s, 9H, Si*Me*$_3$), 3.86 (s, 3H, OC*H*$_3$), 5.48 (s,1H, C*H*), 6.99-6.95 (d, 2H, Ar*H*), 7.46-7.41 (d, 2H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ -0.16 (Si*Me*$_3$), 55.28 (O*C*H$_3$), 63.33 (O*C*H), 119.31 (*C*N), 128.29, 128.47, 131.93, 137.65 (Ar-*C*) ppm.

Compound 14h:



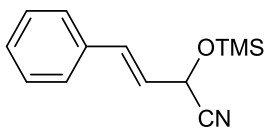
^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 0.19 (s, 9H, Si*Me*$_3$), 5.46 (s,1H, C*H*), 7.49 (d, $^{3}J_{HH}$ = 8.21 Hz, 2H, Ar*H*), 7.65 (d, $^{3}J_{HH}$ = 8.46 Hz, 2H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ -0.43 (Si*Me*$_3$), 62.75 (O*C*H), 113.24 (Ar*C*N), 118.08, 126.82, 132.68, 141.08 (Ar-*C*) ppm.

Compound 14i:



^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 0.11 (s, 9H, Si*Me*$_3$), 5.43 (s, 1H, C*H*), 6.29 (s, 1H, Ar*H*), 6.44 (s,1H, Ar*H*), 7.35 (s, 1H, Ar*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ -0.42 (s, 9H, Si*Me*$_3$), 57.44 (O*C*H), 109.69, 110.78 (Ar-*C*), 117.11 (*C*N), 143.83, 148.28 (Ar-*C*) ppm.

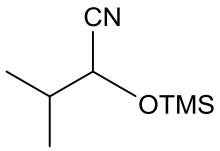
Compound 14j:



^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 0.18 (s, 9H, Si*Me*$_3$), 5.01-5.04(d, $^{3}J_{HH}$ = 5.94 Hz 1H, C*H*), 6.05-6.16 (d, $^{3}J_{HH}$ = 15.79 Hz, 1H, ArC*H*), 6.69-6.77 (m, 1H, CHC*H*), 7.24-7.30 (m, 5H, Ar*H*)

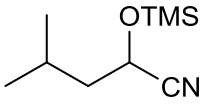
ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 0.98 (Si*Me*$_3$), 62.20 (O*C*H), 118.35 (*C*N), 128.70, 129.05 (*C*H*C*H), 123.55,131.21, 133.91, 135.02, 152.68 (Ar-*C*) ppm.

Compound 14k:



^1H NMR ($CDCl_3$, 200 MHz, 298 K): δ 0.28 (s, 9H, Si*Me*$_3$), 1.10 (d, $^3J_{HH}$ = 6.44 Hz, 6H, CH(C*H*$_3$)$_2$), 2.01 (sept,1H, C*H*(CH$_3$)$_2$), 4.21-4.24 (d, $^3J_{HH}$ = 5.81 Hz, 1H, C*H*) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 1.80 (Si*Me*$_3$), 17.11 (CH(*C*H$_3$)$_2$), 33.76 (*C*H(C*H*$_3$)$_2$), 67.12 (O*C*H), 119.13 (*C*N) ppm.

Compound 14l:



^1H NMR ($CDCl_3$, 200 MHz, 298 K): δ 0.30 (s, 9H, Si*Me*$_3$), 1.02 (d, $^3J_{HH}$ =6.44 Hz, 6H, CH(C*H*$_3$)$_2$), 1.67-1.99 (m, 3H, C*H*C*H*$_2$), 4.50 (t, 1H, C*H*) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 22.31 (*C*H$_3$), 22.41 (*C*H$_3$), 24.03 (*C*H), 44.87 (*C*H$_2$), 59.86 (O*C*H), 120.16 ppm.

6.4.9. Details of DFT computations

All the calculations in this study have been performed with density functional theory (DFT), with the aid of the Turbomole 7.1 suite of programs, using the PBE functional. The TZVP3 basis set has been employed. The resolution of identity (RI), along with the multipole accelerated resolution of identity (marij) approximations has been employed for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. Solvent correction were incorporated with optimization calculations using the COSMO model, with toluene (ε = 2.374) as the solvent. The values reported are ΔG values, with zero point energy corrections, internal energy and entropic contributions were included through frequency calculations on the optimized minima, with the temperature taken to be 298.15 K. The translational entropy term in the calculated structures was corrected through a free volume correction introduced by Mammen et al. This volume correction is to account for the unreasonable enhancement in translational entropy that is generally observed in computational softwares. Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima or transition state structures.

About the Author

Mr. V. S. V. S. N. Swamy, son of Trimurtulu and Nagamani, was born in Pamulaparru village of West Godavari district, Andhra Pradesh, India, in 1989. He completed his B.Sc. Chemistry from D. N. R College, Andhra University. He obtained his master degree from Aditya Degree College, Andhra University. After qualifying CSIR-National Eligibility Test (NET-JRF) examination, he moved to Catalysis Division, CSIR-National Chemical Laboratory, Pune, India to pursue his Ph.D. degree under the guidance of Dr. Sakya Singha Sen. His research interests include the synthesis, reactivity and catalytic applications of low-valent heavier main group 14 compounds.

Education and Research Experience:

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GVK Biosciences Private Ltd: (2012-2013) Trainee Chemist, Hyderabad, India.

M.Sc.: (2010-2012) Chemistry, Andhra University, India

B.Sc.: (2007-2010) Chemistry, D. N. R College, Andhra University

List of Scientific Contributions:

Publications

1. Cations and dications of heavier group 14 elements in low oxidation state; **V. S. V. S. N. Swamy**, S. Pal, S. Khan, S. S. Sen, *Dalton Trans.*, **2015**, *44*, 12903–2923.

2. Benz-amidinato stabilized a monomeric calcium iodide and a lithium calciate(II) cluster featuring group 1 and group 2 elements; S. Yadav, **V. S. V. S. N. Swamy**, R. G. Gonnade, S. S. Sen, *ChemistrySelect.*, **2016**, *1*, 1066–1071.

3. Facile access to a Ge(II) dication stabilized by isocyanides; **V. S. V. S. N. Swamy**, S. Yadav, S. Pal, T. Das, K. Vanka, S. S. Sen, *Chem. Commun*., **2016**, *52*, 7890–7892.

4. Metal free mild and selective aldehyde cyanosilylation by a neutral penta-coordinate silicon compound; **V. S. V. S. N. Swamy,** M. K. Bisai, T. Das, S. S. Sen, *Chem. Commun*., **2017**, *53*, 6910–6913.

5. C(sp^3)–F, C(sp^2)–F and C(sp^3)–H bond activation at silicon(II) center; **V. S. V. S. N. Swamy,** N. Parvin, K. V. Raj, K. Vanka, S. S. Sen, *Chem. Commun.*, **2017**, *53*, 9850–9853.

6. Facile activation of Si–H bond by an electrophilic carbene; **V. S. V. S. N. Swamy,** G. Kundu, S. S. Sen*, J. Indian. Chem. Soc.*, **2018***, 95*, 789–793.

7. Silylene induced cooperative B–H bond activation and unprecedented aldehyde C–H bond splitting with amidinate ring expansion; **V. S. V. S. N. Swamy**, K. V. Raj, K. Vanka, S. S. Sen, H. W. Roesky, DOI: 10.1039/c9cc00296k.

8. Synthesis and reactivity of a super silyl silylene; M. K. Bisai, **V. S. V. S. N. Swamy**, T. Das, R. G. Gonnade, K. Vanka, S. S. Sen, Communicated.

Symposia Attended

National conferences: 1 (Poster presentation)

2 (Participation)

International conferences: 1 (Oral presentation)

2 (Participation)