A Review on N-Heterocyclic Carbene Supported Halosilylene

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By

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Declaration

I hereby declare that the matter embodied in this report is the result of investigation carried out by me in the Department of Chemistry, Indian Institute of Technology Hyderabad under the supervision of ***Dr. G. Prabusankar***.

In keeping with general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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Abstract

This literature survey is associated with the highly useful compound NHC supported halosilylenes. Silylenes are the silicon analogues of singlet carbenes, are highly reactive compounds with dicoordinate divalent silicon atoms. They are the silicon counterparts to carbenes and plays a very important role in silicon chemistry. Parent silylene and its derivatives R_2Si: with small organic groups R represent reactive intermediates (generally formed *in-situ*), which have been investigated in the gas-phase, in diluted solutions, and in frozen rare-gas matrices at low temperatures. Prior to 1994, silylenes existed only as reactive intermediates (generally formed *in-situ*), isolable only in low-temperature matrixes. The field of stable silylene research has grown dramatically since the first isolation of a stable N-heterocyclic silylene by West *et al.* in 1994. Since then, several stable halosilylenes have been synthesized, some in fact showing remarkable thermal stability. NHC has a carbon centre with a lone pair of electrons. Carbon donates its lone pair of electron and binds strongly with silicon in low oxidation state making it stable enough to be isolated. The bond formed is yet facile enough to break for the use of monomeric SiX_2 under specific reaction conditions. They are isolated in varying crystalline form with different thermal stabilities depending on the NHC and silicon halide used. My work highlights the synthesis of such NHC supported halosilylenes, their reactions to make several silicon analogues of carbon compounds, Si-Si multiple bond, Si-E (E = main group element, transition metal) bonds, etc., and their characterization using 1H NMR, 13C NMR, 29Si NMR and molecular & electronic structural analysis using X-ray and computational methods as DFT Turbomole at BP/TZVP.

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Chapter 1

Introduction

Silylene is a molecule with a divalent neutral silicon(0) atom having a lone pair of electrons. They are the silicon counterparts to carbenes and plays a very important role in silicon chemistry [1]. Parent silylene and its derivatives R_2Si: with small organic groups R represent reactive intermediates (generally formed *in-situ*), which have been investigated in the gas-phase, in diluted solutions, and in frozen rare-gas matrices at low temperatures. With the advent in the carbene chemistry, many isolable carbenes were synthesized and characterized. *Arduengo*, in 1991 isolated the first free carbene. NHC (N-Heterocyclic carbene) is one kind of isolable carbene. N-Heterocyclic carbenes (NHCs) are cyclic carbenes attached with α-amino substituents [40]. Strong σ-donors, have reactivities like other classical 2 electron donors (phosphines, amines, ethers). NHCs can stabilize the low valent and high valent transition metals, main group elements, and lanthanides [2]. Because of their lone pair and vacant orbital, singlet carbenes can, in theory, act as either Lewis acids or Lewis bases. The electronic factors stabilize the NHC and make it isolable. NHCs are exceptionally good σ donors so form strong metal–carbon bonds (thus stable Si-C bond) [3]. Singlet carbenes of NHCs are distinct Lewis bases that show both π basicity and σ acidity. Electronic factors operating in both the π and σ frameworks result in a "push-pull" synergistic effect to stabilize the carbene. π donation into the carbene from the out-of-plane π orbital stabilizes electrophilic reactivity and σ withdrawal by electronegative atoms stabilizes nucleophilic reactivity. The combined effect is to increase the singlet-triplet gap and stabilize the singlet-state carbene over the more reactive triplet-state carbene.

While, carbenes are observed in either the triplet or singlet state depending on the nature of the substituents, silylenes typically have a singlet ground state because the energy gap between the 3s and 3p orbitals of the silicon atom is very large and so the singlet-triplet gaps are enormous. The lone pair of eletron is present as HUMO and the empty *p* orbital as LUMO in singlet ground (^1A) state. Thus they can act as both Lewis acid (electrophilic) and Lewis base (nucleophilic) depending on the substituents [11]**.** They are key intermediates in many thermal, photochemical and metal reduction reactions of organosilicon compounds.

Likewise, dichlorosilylene ($:SiCl_2$) is an elusive divalent silicon species, which plays a particular role in the Siemens process, in the chemical vapor deposition of thin silicon films, and in dry etching of silicon wafers by elemental chlorine, as well as in the plasma etching of silicon and silicon dioxide interfaces. Although synthesis and reactivity of gaseous $:SiCl_2$ has been investigated since 1964, studies on its reactivity have been limited to the gas phase and matrix-isolation systems at low temperatures (77 K), because it polymerizes readily to $(SiCl_2)_n$ at higher temperatures.

Since 1994, the concept of donor–acceptor stabilization has been very successfully applied to the synthesis of several types of isolable cyclic and acyclic silylenes. Recent progress includes the striking synthesis of stable H_2Si: complexes, reported by Rivard, Robinson, and their respective co-workers [1]. Since then, several stable halosilylenes have been synthesized, some in fact showing remarkable thermal stability. NHC has a carbon centre with a lone pair of electrons. Carbon donates its lone pair of electron and bonds strongly with silicon in low oxidation state making it stable enough to be isolated [4]. They are electronically stabilized by the amino group and sterically protected by the attached bulky group. The aromatic π-electron delocalization on the silicon containing ring gives additional stability to the system. The bond formed is yet facile enough to break for the use of monomeric SiX_2 under specific reaction condition [5]. They are isolated in varying crystalline form with different thermal stabilities depending on the NHC and the siliconhalide used. So, these complexes can act as electron donor to transition metals and lanthanides and hence are unique ligands which can collectively act as catalysts [6]. In 2009, the research groups of Roesky and Filippou showed that dihalosilylenes $:SiX_2$ (X=Cl, Br) can be stabilized by N-Heterocyclic carbenes (NHCs) to form isolable NHC-SiX_2. The latter represent long-sought convenient dihalosilicon(II) precursors.

They are key intermediates in many thermal, photochemical and metal reduction reactions of organosilicon compounds. They are used in many reactions which involves introduction of Silicon to it. NHC-SiX_2 and its derivatives undergoes many reactions including electrophilic and nucleophilic reactions, Lewis acid base attack and many more [7]. The unstable and rare silicon double bond (silylidene) and triple bond (silylidyne) compounds are also made using it. It also facilitates the formation of chlorosilyliumylidene chloride and chlorosilathonium complex which is of much use and is hard to make. There are many more reactions and uses of NHC-SiX_2. All these complexes are characterized and optimised using NMR, IR, X-Ray Diffraction and Computational studies.

Chapter 2

Synthesis of NHC based Halosilylene

2.1 Introduction

Silicon dihalides are the silylenes with unusual +2 oxidation state. They generally polymerises as $(SiX_2)_n$ known as polymeric perhalopolysilane. These are highly unstable with respect to its dispropotionation products.

$$2\ SiX_2\ (II) \longrightarrow Si(0) + SiX_4\ (IV)$$

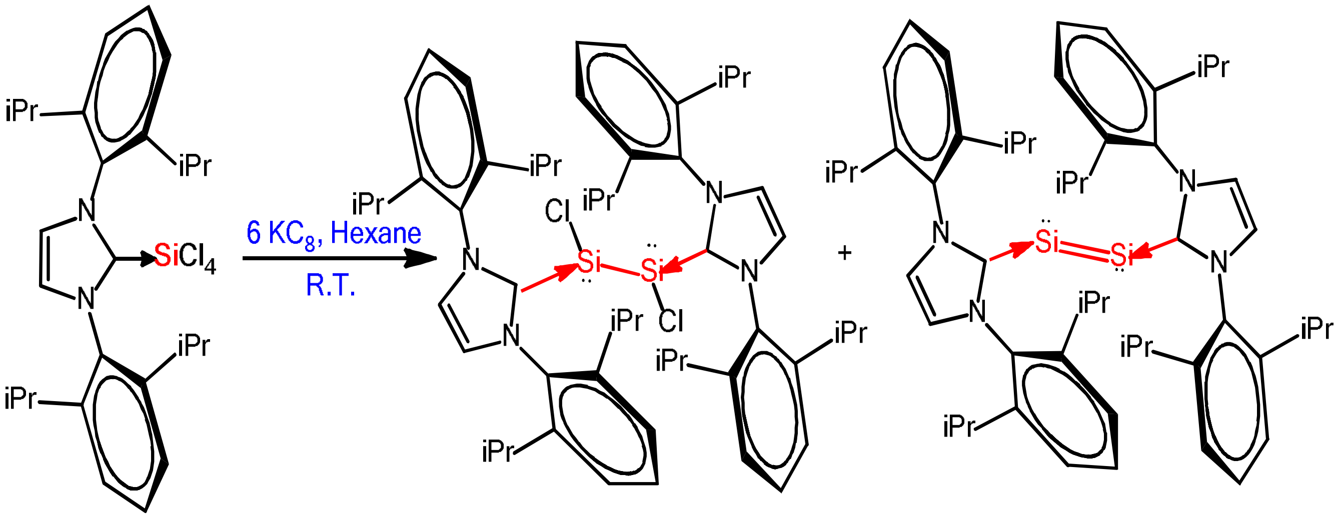
SiX_2 are used in the chemical transport of silicon in many reactions. So, attempts are made to isolate monomeric silicon dihalide or its equivalent that can be handled at room temperature. Silicon in SiX_2 has six valence electron. The two unpaired electron and one vacant p-orbital make it very reactive. Thus the isolation became a challenge. After the isolation of first NHC-SiR_2 by West et al. many NHC supported monosilylenes were isolated. Silicon dihalides were also stablized using NHC and different studies are being carried out on them. Structural and bonding aspects are also studied with there characterisation from many techniques to get a more clear detail about the NHC-SiX_2. Carbene carbon in NHC donates its lone pair of electron via σ donation to the vacant orbital of silicon forming a strong bond. The lone pair of electron on Silicon is yet available for further donation and is stereochemically active, which results in its reactivity. The bond thus formed is stable enough to be isolated as crystals and is labile enough for further reactions. The NHC-SiX_2 acts as the monomer of SiX_2 liberating it in certain reaction conditions. The stablility depends on the NHC and silicon halide involved.

$$NHC + SiX_4 \xrightarrow[KC_8,\ RT]{Solvent} NHC\text{-}SiX_2 + 2\ KX$$

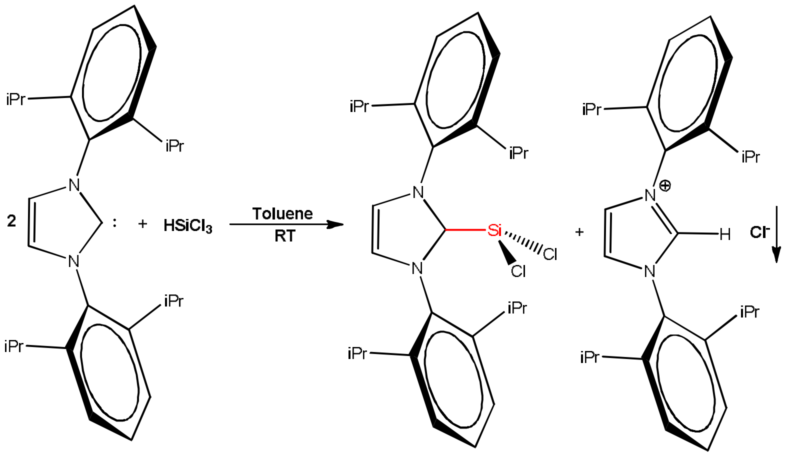
The general way of synthesising any silylene/ low valent Si compounds is to take parent compound with respective NHC in presence of a strong reducing agent (generally potassium graphite KC_8. The reactions are carried out at room temperature. The solvent used are toluene, benzene or THF depending on the solubility of SiX_2.

2.2 Literature Review

The first non-isolable dichlorosilylene was trapped by Jung *et al.* Later Kuhn *et al.* in 1995 prepared N-heterocyclic carbene (NHC) adduct of $SiCl_4$. After this Robinson *et al.*, in 2008 introduced carbene stabilised bis silylene (Si→ +1 oxidation state) using L^1SiCl_4 (L^1 = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene). L^1SiCl_4 on reduction with potassium graphite (KC_8) in 1:6 molar ration in hexane gives orange-red, sheet like crystals of $L^1ClSi\text{-}SiClL^1$ (**Si1**) with 6.1% yield (Scheme 1) [8]. The complex is air sensitive. The 1H NMR of imidazole ring resonates at δ 6.31 ppm. $^{29}Si\{^1H\}$ NMR peak is at δ 38.4 ppm in C_6D_6. The X-ray analysis shows that (Cl)Si-Si(Cl) core is sterically well shielded with L^1 ligand. The silicon centre is in three-coordinated trigonal pyramidally coordinated geometry. The Si-Si bond distance is 2.393(3) Å which is only 0.03 Å longer than the usual Si-Si single bond. The Si-C bond distance (average) is 1.934(6) Å and Si-Cl bond distance is 2.164(3) Å comparable to the sum of covalent radii of Si and Cl (2.16 Å).

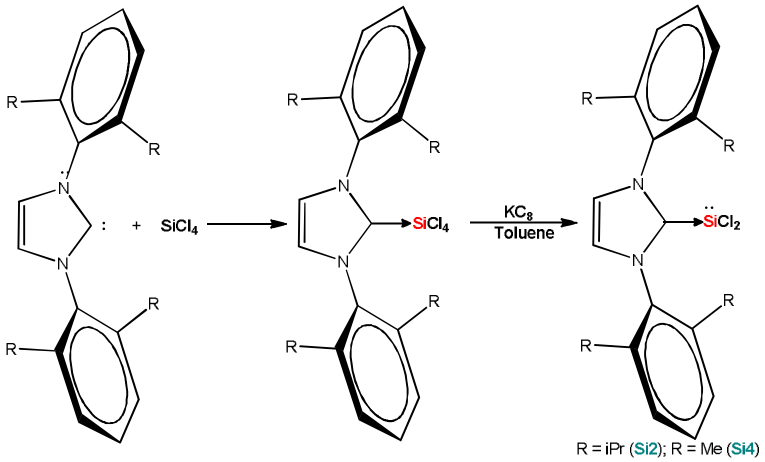


Scheme 1. Synthesis of $L^1ClSi\text{-}SiClL^1$ (**Si1**)[8]



Scheme 2. Synthesis of L^1SiCl_2 (**Si2**)[9]

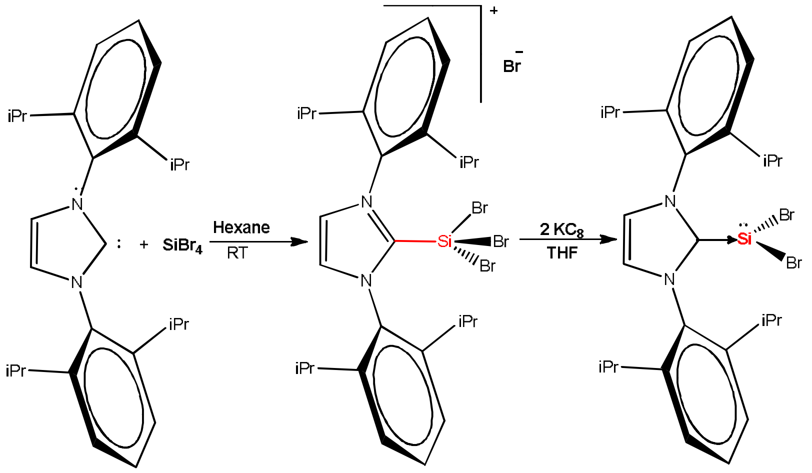
The first base stabilised dichlorosilylene, stable at room temperature is L^1SiCl_2 (**Si2**), synthesised by Roesky *et al.* in 2009. It is formed under mild reductive elimination of HCl from $HSiCl_3$ in presence of NHC (L^1) in toluene affording 79% yield (Scheme 2) [9]. A multistep procedure was made to prepare L^1SiCl_2 (**Si2**) and L^2SiCl_2 (L^2 = 1,3-bis(2,4,6-trimethylphenyl) imidazole-2-ylidene) (**Si4**) using L^1SiCl_4 with 2 equivalents of potassium graphite (KC_8) in toluene to make L^1SiCl_2 (**Si2**) and L^2SiCl_2 (**Si4**), respectively (Scheme 3)[9].



Scheme 3. Synthesis of L^1SiCl_2 (**Si2**) and L^2SiCl_2 (**Si4**)[9]

L^1SiCl_2 (**Si2**) is colourless crystals obtained in toluene at -35°C in 48% yield, whereas L^2SiCl_2 (**Si4**) is pale yellow solid from a mixture of toluene and n-hexane (2:1). Both are soluble in THF and toluene. Molecular structure of L^1SiCl_2 (**Si2**), determined by Single Crystal XRD is monoclinic with space group $P2_1/c$. **Si2** is slightly distorted trigonal pyramidal geometry at Silicon atom with stereochemically active lone pair in the contact Lewis acid-base pair. The sum of the bond angles at the silicon atom in **Si2** (289.74°; compare with 291.08° in the gasphase optimized structure). The molecular simuation on **Si2** by DFT Turbomole at BP/TZVP gave the angles between LP_{Si}-Si-C(carbene), LP_{Si}-Si-Cl(in-plane) and LP_{Si}-Si-Cl(orthogonal) are 114.408, 121.938 and 123.378, respectively (LP_{Si} ; lone pair density).

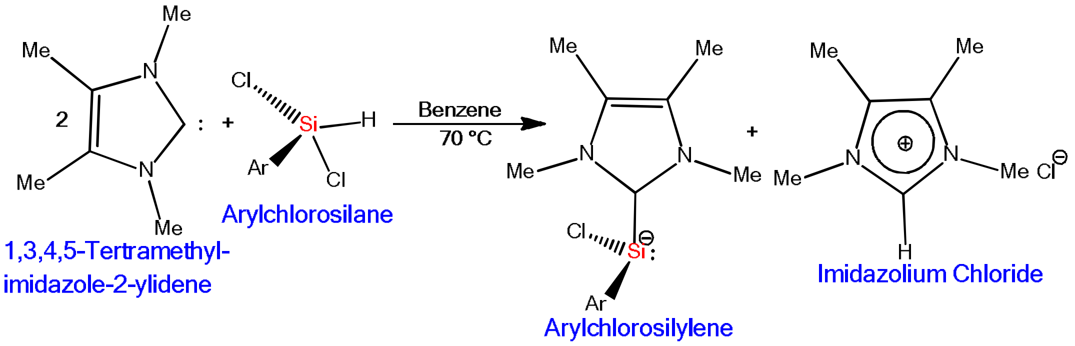
The first stable carbene adduct of dibromosilylene - L^1:$SiBr_2$ was isolated by Alexander *et al.* in 2009 .The synthesis is a two-step reaction in which first $SiBr_4$ reacts with one equivalent of L^1: in hexane at RT giving an ionic product $[SiBr_3(Idipp)]^+Br^-$; isolated as white solid with high yield then reaction with 2.5 equivalent of potassium graphite (KC_8) in THF at ambient temperature gives the L^1:$SiBr_2$ (**Si3**) (Scheme 4)[10].



Scheme 4. Synthesis of L^{1}SiBr$_2$ (**Si3**)[10]

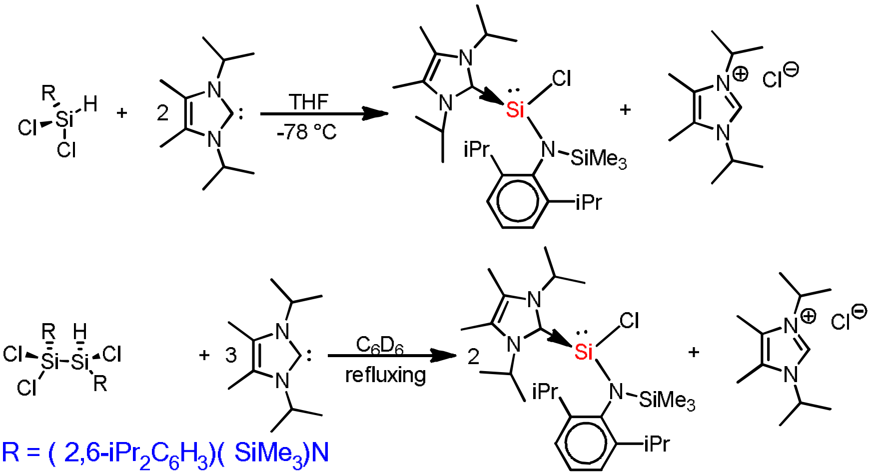
Si3 is isolated as yellow air sensitive solid with 48% yield and is stable in inert benzene solution at ambient temperature for at least one week. The crystal structure of **Si3** shows Silicon centre is trigonal pyramidal (sum of angles at Si=292.7°) indicating the presence of stereochemically active lone pair of electron on Si. The Si-C bond length; being 1.989(3) Å; is between silylene carbene adduct (2.162(5) Å) and silenes (1.702(5) Å), represents a strong C→Si donor acceptor single bond.

Filippou *et al.*, in 2010, made the first stable carbene adduct of arylchlorosilylene, SiArCl(ImMe$_4$) using the electronic stabilization effect of NHC. They added two equivalents of 1,3,4,5-Tertramethylimidazole-2-ylidene to the solution of arylchlorosilane, SiArHCl$_2$, in benzene at 70 °C (Scheme 5)[12] to give the product. The Ar group can be C$_6$H$_3$-2,6-Mes$_2$ (Mes = C$_6$H$_2$-2,4,6-Me$_3$) (**Si5**) synthesized or it can be C$_6$H$_3$-2,6-Trip$_2$ (Trip = C$_6$H$_2$-2,4,6-iPr$_3$) (**Si6**).



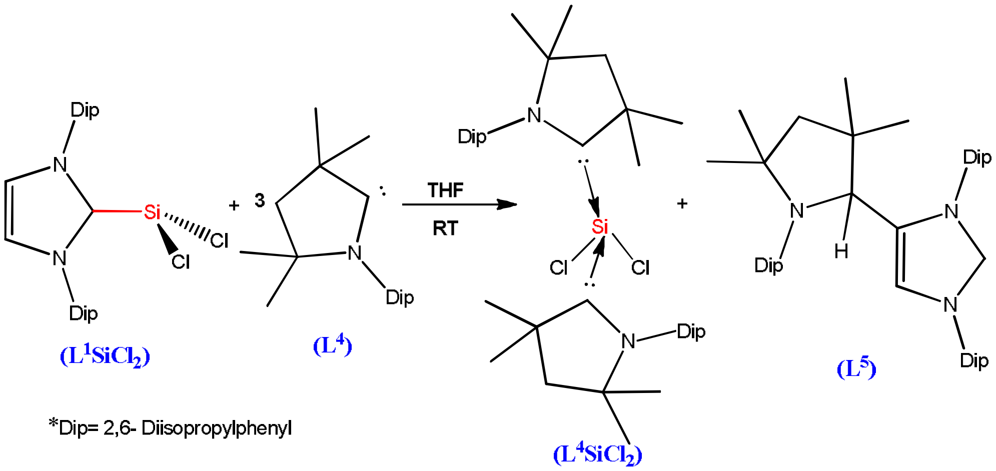
Scheme 5. Synthesis of SiArCl(ImMe$_4$) (**Si5** & **Si6**)[12]

Si5 and **Si6** are isolated as yellow air sensitive solid solid with 72% and 93% yield respectively. Si4 is starts decomposing in 24 h and Si5 is stable for atleast 120 h in inert benzene at ambient temperature. The ^{13}C NMR peaks are at δ 165.2 ppm for **Si5** and δ 166.7 ppm for **Si6**. For aryl C, the value is δ 150.6 ppm for both. The ^{29}Si{^{1}H} NMR of **Si5** is at δ 1.34 ppm and **Si6** is at δ 0.77 ppm; which is slightly upfield shifted than **Si2**. In **Si5** the carbene carbon is in trigonal planar coordinated geometry with sum of all angle 357.9°. Si-$C_{carbene}$ bond distance is 1.963(2) Å and Si-C_{Ar} bond distance is 1.937(2) Å. Also, Si-Cl bond distance is 2.1836(8) Å which is comparable to **Si2**.



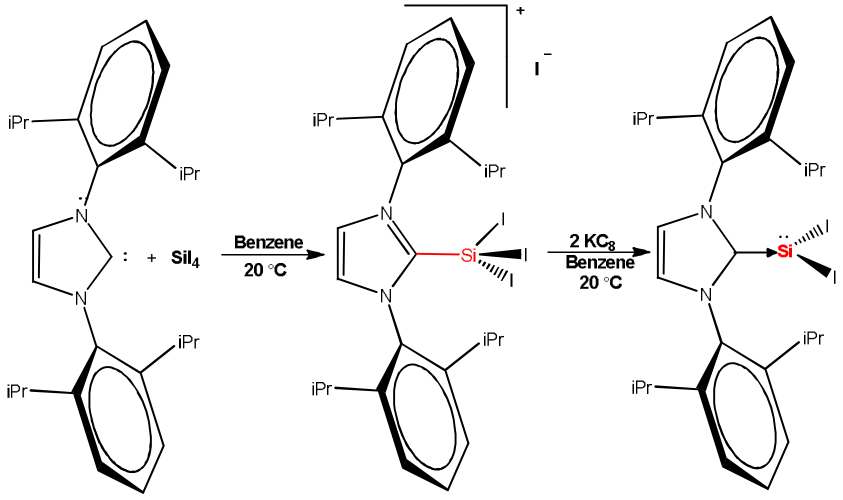
Scheme 6. Synthesis of NHC stabilised aminochlorosilylene (**Si7**)[23]

In 2011, Cui *et al.*, prepared the first donor stabilised aminochlorosilylene under optimised conditions. They reacted aminochlorosilane, $RSiHCl_2$ and dilsilane, R_2SiHCl_3 (R = (2,6-$i$$Pr_2C_6H_3$)($SiMe_3$)N) with NHC to make the product. They treated, first, $RSiHCl_2$ with 2 equivalents of I$i$$Pr_2$ (1,3-bis(isopropyl)-imidazol-2-ylidene) in THF at low temperature and R_2SiHCl_3 with 3 equivalents of I$i$$Pr_2$ to yield the same yellow powdered product (**Si7**) with 75% yield (Scheme 6) [23]. The ^{29}Si NMR give its resonance peaks at δ 3.14 ppm which is downfield than Si4 and Si5 (δ 0.77 to 1.34 ppm). The ^{13}C NMR peak is at δ 164.08 ppm. The silicon centre is trigonal pyramidal, three-coordinated with sum of all angles being 305.22°. The Si-$C_{carbene}$ bond distance is 2.0023 Å which is slightly longer than the other NHC stabilised silylenes.



Scheme 7. Synthesis of $L^4{}_2SiCl_2$ (**Si8**)[32][33]

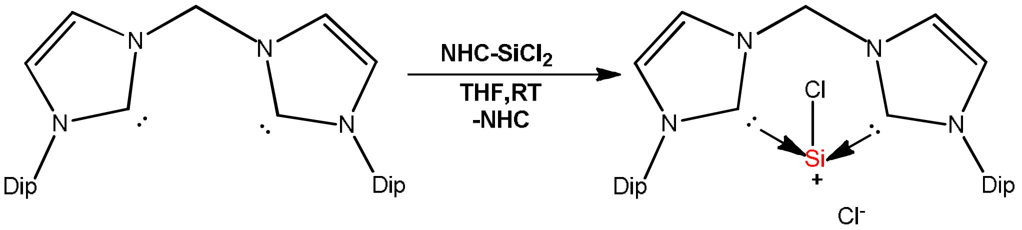
In 2013, Roesky *et al.* reported substitution reaction (exothermic) for the synthesis of more stable biradical. First, L^1SiCl_2 is synthesised (Scheme 2) followed by the synthesis of L^4SiCl_2 (**Si8**) and L^5 (Scheme 7)[32][33] ,where L^5 is the biproduct formed due to the slow reaction between free L^1: and $L^{4:}SiCl_2$; prism like crystals. L^4_2:$SiCl_2$ is isolated as two crystalline polymorphs differing only in size of unit cell, having nearly identical geometries according to crystallization conditions. Polymorph II of dark blue block crystals is formed at 0 °C or RT in 2-3 days in the mother liquor and is stable enough on exposure to air for one week (powdered form for 2-3 days) and do not decomposes at RT in inert atmosphere for 3-4 months. It melts at 179-181 °C and decomposes at 185-186 °C. Polymorph I of lighter blue block crystals is formed at 0 °C in 1-2 weeks in the mother liquor and are stable in the mother liquor in inert condition for a few weeks and decomposes soon in 2-3 days to colourless crystals (solid form do not decomposes in refrigerator at 0 to -32 °C). It melts at 167-168 °C and decomposes at 172-173 °C. **Si8** crystallises in monoclinic space group *C2/c*. The geometry is distorted tetrahedral and the bond angle of carbene C-Si-C widens to 122.99(7)° due to steric factors. The ^{29}Si-NMR signal at δ 4.13 ppm(in dilute solution only; δ 19.06 ppm for **Si2**) shows intermolecular forces are quenching the NMR resonance and indicates radical nature of compound.



Scheme 8. Synthesis of L^1SiI_2 (**Si9**)[35]

The synthesis of first diiodosilylene was reported in 2013 by Alexander *et al.* which was similar to **Si3** synthesis. SiI_4 is treated with L^1 in benzene at 20 °C to make $[SiI_3(Idipp)]^+I^-$, which on further treatment with 2.3 equivalents of KC_8, in benzene at 20°C gives **Si9** with yield ~81% (Scheme 8)[35]. **Si9** is stable in benzene and toluene at ambient temperature for many days and decomposes in solid state above 160 °C. X-Ray crystallography shows its structure is similar to its Cl and Br analogues and has trigonal pyramidal coordinated Silicon centre showing stereochemically active lone pair's presence. The Si-I bond length is 2.575(3) Å which is longer than that in the SiI_4

(2.432(5) Å). The Si-C(carbene) bond length is 1.984(7) Å which is similar for Si1 (1.989(3) Å) and Si2 (1.985(4) Å). Also, the bond energies for **Si9** (121.4 kJ/mol), **Si2** (121.4 kJ/mol) and **Si3** (123.6 kJ/mol) shows relatively stronger donor acceptor bond. The ^{29}Si{^{1}H}-NMR are δ -9.7 ppm for Si9, δ 10.9 ppm for Si3 and δ 19.06 ppm for Si2 displays the same ^{29}Si nucleus deshielding upon halide substitution (I→Br→Cl).



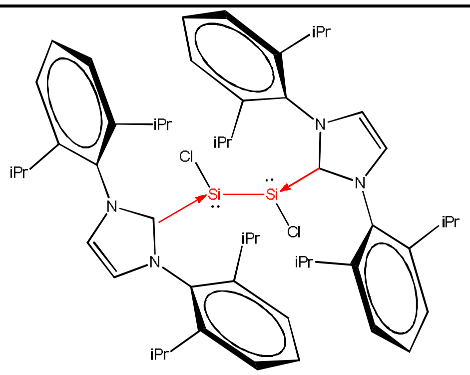
(L^6) **([L^6SiCl]$^+$Cl$^-$)**

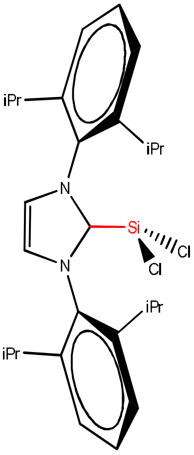
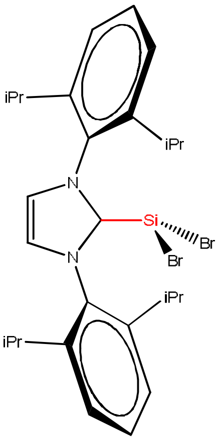
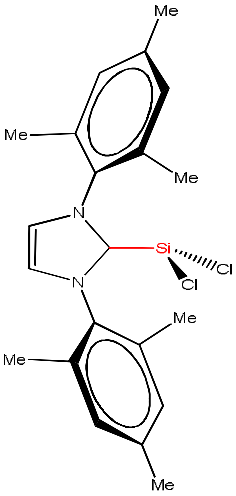
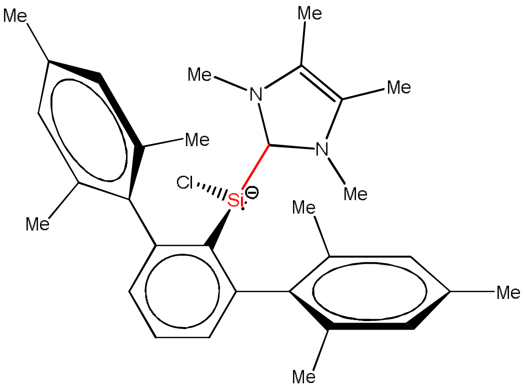
Scheme 9. Synthesis of L^6SiCl_2 (**Si10**)[36]

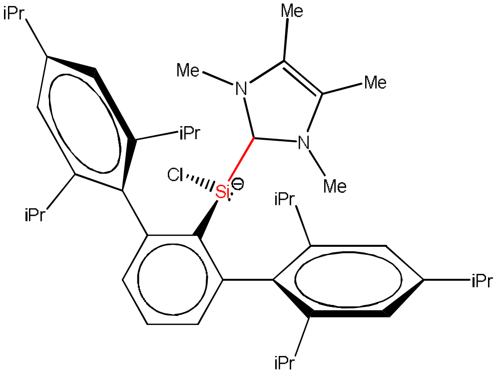
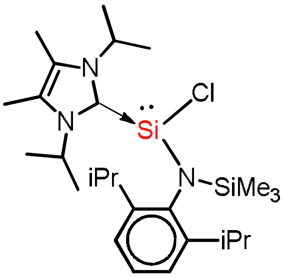
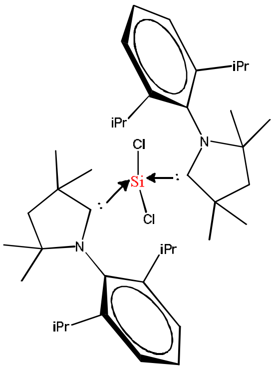
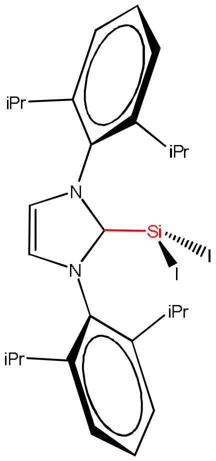
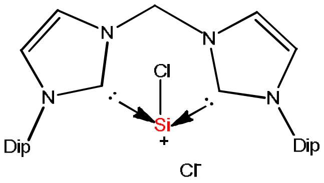
Same year, in 2013 Driess et al. synthesised bis NHC stabilised silylones. The bis NHC (L^6) on reaction with NHC-$SiCl_2$ in THF at RT gives **Si10**. **Si10** is insoluble in THF but is soluble in acetonitrile and is isolated with 57% yield (Scheme 9)[36]. Silicon centre is trigonal bipyamidally coordinated with two carbene carbon and one Cl. The counter anion Cl^- is separated with the smallest distance of 6.424(2) Å from the silicon centre. There is drastic upfield shift of the ^{29}Si peak i.e δ -58.4 ppm showing much stronger electron donation effect by chelating bis NHC ligand (A). The Si-C bond distance is 1.961(4) Å, which is normal.

Table 1

Key features of structurally characterized molecules consist of C_{NHC} Si bond

Molecule	Compound No.	^{13}C NMR of NCN, δ ppm	^{29}Si NMR of C-Si, δ ppm	C-Si separation, Å	Reference
	(Si1)	unknown	38.4	1.934(6)	[8]

	(Si2)	unknown	19.06	1.985	[9]
	(Si3)	164.5	15.8	1.989(3)	[10]
	(Si4)	unknown	17.84	Unknown	[9]
	(Si5)	165.2	1.34	Unknown	[12]

	(Si6)	166.7	0.77	1.963(2)	[12]
	(Si7)	164.08	3.14	2.0023	[23]
	(Si8)	210	4.13(only in dilute solution)	1.879	[32],[33]
	(Si9)	unknown	-9.7	1.984(7)	[35]
	(Si10)	unknown	-58.4	1.961(4)	[36]

Chapter 3

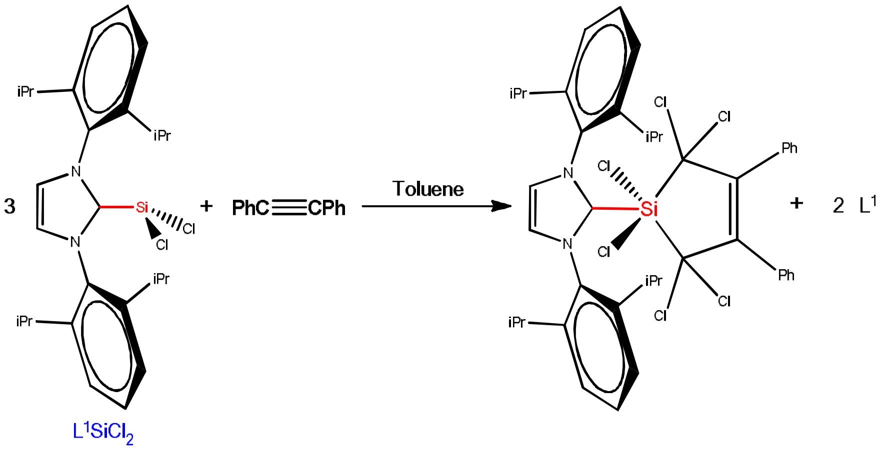
Reactions with NHC supported Halosilylenes

3.1 Introduction

Silylenes and Halosilylenes serves a widespread role in many reactions for many difficult and rare synthesis. The NHC-$SiCl_2$ kind complexes are expected to be the structural motifs which are related to free $SiCl_2$. Since they are good source of divalent silicon, stable compounds having Si-C, Si-M (M=Main Group, Transition Metal), Si=Si multiple bonds can be formed easily. Rare compunds like small rings systems with high ring-strain energy containg silicon (silaoxirane), C4-silyl substituted NHC, dichlorosilamines (Si=N), silaisontriles , trisilaallenes (silicon analogue of allene) etc are very suitably made using NHC stabilised silylenes. The halogen can be replaced to hydrogen (silahydride). Compounds which exists in gas phase only (e.g. $[ClSi:]^+$, silacarbonyl halide) are also synthesized. The reason behind such reactivity is the presence of active lone pair on Silicon centre and the stability imposed by NHC. The halosilylene are ambiplic in nature. It accepts the carbene electron pair (electrophile) and have one lone pair of electron on Si. This can be donated. This propertry is used in making adducts with main group element which have vacant orbital to accept the electron pair. Both the acceptor bond (C→Si) is much polar (hard ligand) than the donor bond (Si→B) which is covalent (soft ligand). This formed compound can be used to make Si-E (metal, O) bond by replacing Boron. Similar type of reaction are used in making Si-M (transition metal) bonds.

3.2 Reaction of NHC:SiX$_2$ (X = Cl,Br,I,R) with Organic Substrate

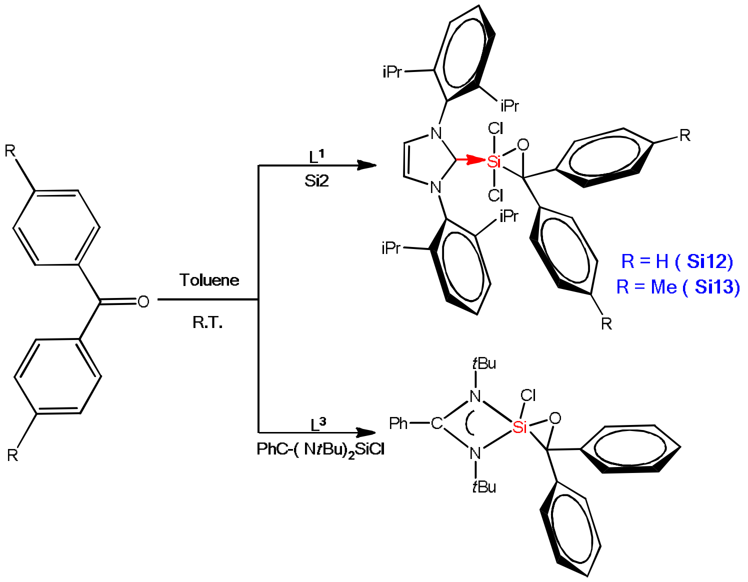
The NHC-SiCl$_2$ kind complexes are expected to be the structural motifs which are related to free SiCl$_2$. This lability of NHC-SiCl$_2$ to liberate NHC and SiCl$_2$ was first demonstrated by Roesky *et al.* in 2009 by the reaction of **Si2** with excess of diphenylacetylene in toluene for the generation of **Si11** (Scheme 10)[9].



Scheme 10. Reaction of L^{1}SiCl$_2$ (**Si11**)[9]

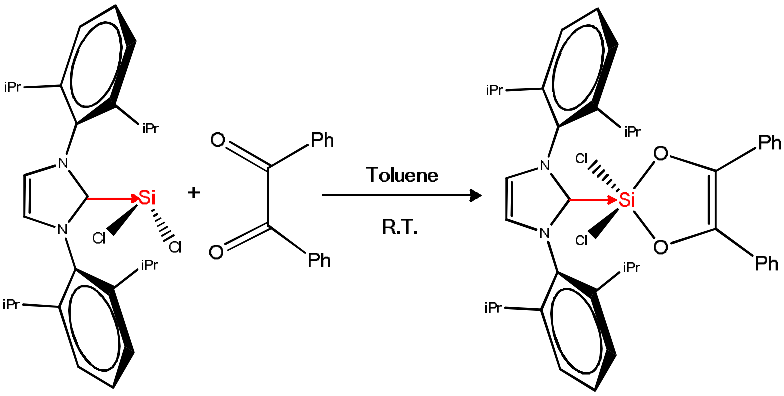
Si11 crystallizes in triclinic space group $P\bar{1}$ with toluene as lattice solvent. It has a five membered Si$_3$C$_2$ ring with three SiCl$_2$ moieties. One silicon is *penta* -coordinated with two chlorine atoms occupying the axial position of a distorted trigonal bipyramidal polyhedron. Equitorial positions are occupied by two adjacent silicon and carbene carbon of L^1(NHC). Si-Ccarbene bond distance is 1.911(17) Å. The other two silicon of ring are in distorted tetrahedral environment. Si-Si bond distance (mean) is 2.323 Å (similar to α-Silicon, 2.36 Å). Si-Cl bond distance for SiCl$_2$ coordinated to L^1(NHC) is 2.254(7) Å which is slightly longer than L^1(NHC) free SiCl$_2$ *i.e.* 2.047(7) Å. The ^{29}Si NMR peaks are at δ -2.84 and -142.47 ppm.

Silicon carbon bonds can be formed by reacting silylenes with organic substrates. Small rings systems with high ring-strain energy containg silicon (silacyclopropane and silacyclopropene) are very reactive and are used to make organosilicon compunds. Silaoxiranes are three membered ring with one silicon, oxygen and carbon each. Its isolation was very difficult and was achieved in 2010 by Roesky *et al.* by the reaction of Si2 (dichlorosilylene) with ketone in toluene (**Si12 and Si13**) and the reaction of ketone with PhC-(N*t*Bu)$_2$SiCl (**L**^{3}-monochlorosilylene) (**Si14**) to make stable silaoxirane (Scheme 10) [13] . These silaoxiranes are electronically stabilised by neutral σ-donor (NHC).



Scheme 11. Reaction of L^{1}SiCl$_2$ (**Si12 & Si13**)and L^3 (**Si14**) with ketone [13]

Also they prepared 2,5-dioxa- 1-silacyclopent-1-enes were prepared by reaction of a stable silylene (thermally or photochemically synthesised) with diketones (**Si15**) (Scheme 12) [9].



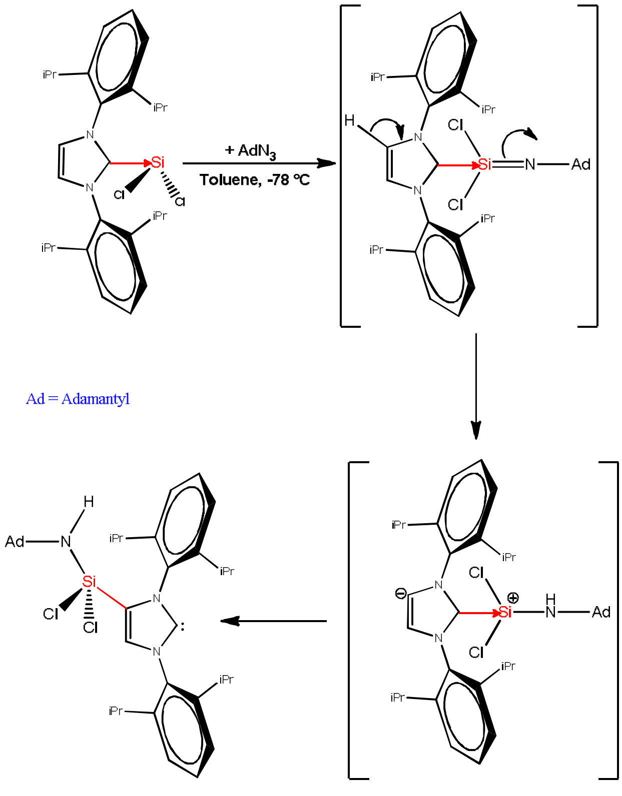
Scheme 12. Reaction of L^{1}SiCl$_2$ with diketone (**Si15**) [13]

Si12, Si13, Si14 and Si15 are all colourless crystals with pentacoordinated silicon centre. They are stable in inert atmosphere and soluble in common organic solvents. ^{1}H NMR of Si12, Si13 and Si15 show one set resonance for NHC ligand and Si14 show two resonances for the amidinate moiety. And all shows signals for phenyl group attached to OSiC or O$_2$SiC$_2$ ring. ^{29}Si NMR displays sharp signals at δ -123.85, -123.39, -115.53 and -99.50 ppm for Si12, Si13, Si14 and Si15 respectively.

Si12 crystallises in monoclinic space group $P2_1$/c with one toluene molecule in asymmetric unit and Si13 in the orthorhombic space group *Pbca* with half molecule of n-hexane in asymmetric unit and distorted trigonal-bipyramidal geometry. In both NHC occupies axial position. C→Si bond length is

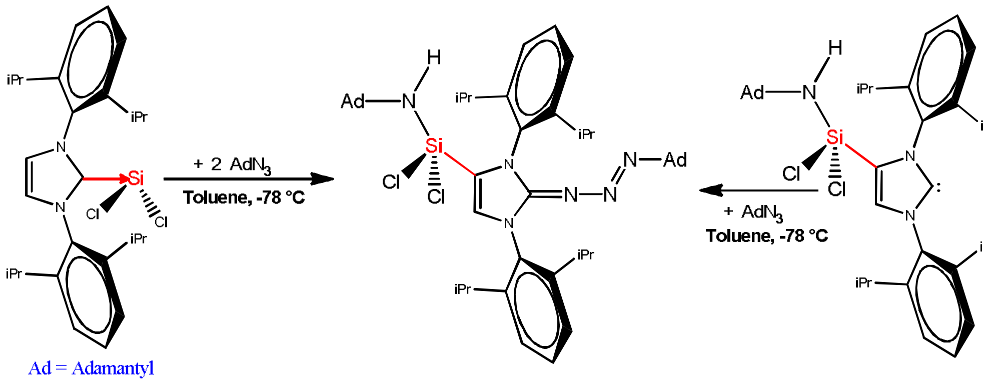
1.9653(15) Å in Si12 and 1.9724(17) Å in Si13. Si-Cl bond is relatively shorter in both than Si2. Si-O bond in Si12 (1.6520(10) Å) and Si13 (1.6486(13) Å) are slightly shorter than reported silaoxirane may be due to presence of electronegative chlorine. Si14 crystallises in monoclinic space group $P2_1$/c and appears in distorted square-pyramidal geometry. The Si-O and Si-C bond distances are 1.6534(13) Å and 1.8641(19) Å, respectively. Si-Cl bond length is 2.0108(6) Å which is shorter than L^3 (2.0156(1) Å). Si15 crystallise in monoclinic space group $P2_1$/c with two molecules in asymmetric unit and have trigonal-bipyramidal geometry. One Cl has axial and one Cl has equatorial arrangement with bond length 2.2034(8) Å and 2.0814(8) Å, respectively. C→Si bond distance is 1.939(2) Å.

Roesky *et al.* in same year, 2010, synthesised abnormal C4-silyl-substituted NHC (**Si16**) by oxidative addition and C-H activation of Si2 with 1-azidoadamantane (AdN_3) at -78 °C in toluene (Scheme 13) [17] showing the unique reactivity of NHC-stabilized dichlorosilylenes.



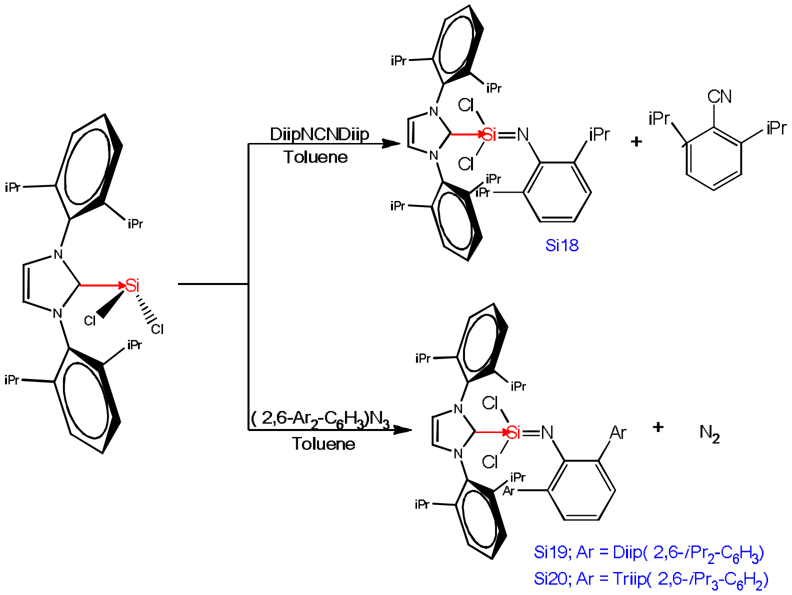
Scheme 13. Reaction of L^1SiCl_2 with N_3Ad (**Si16**) [17]

It is isolated as colourless crystals with 87% yeildand high stability and they can be handled in air. This is due to electronic properties of carbene atom. ^{1}H NMR of Si16 appears at δ 7.45 ppm for backbone proton, δ 1.08 ppm for IPr and δ 2.61 ppm for amino proton. ^{13}C NMR peak of carbene carbon is at δ 224.21 ppm showing different NHC formation. ^{29}Si NMR resonance is at δ -30.01 ppm. It crystallizes in triclinic space group *P*-1with one toluene in asymmetric unit.



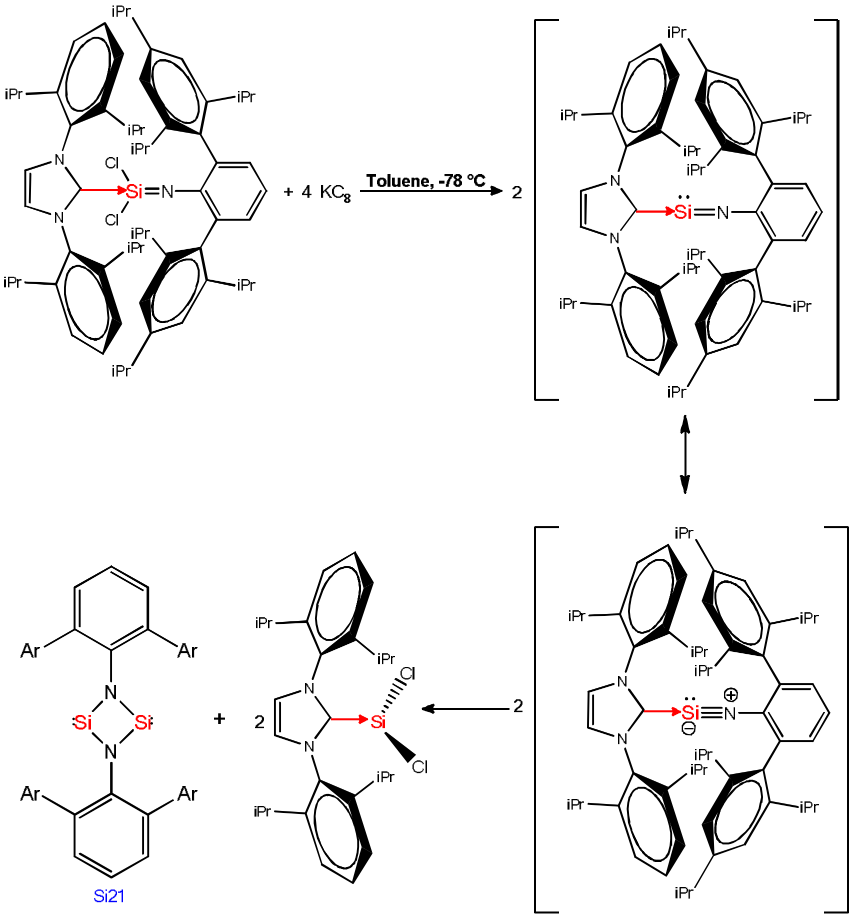
Scheme 14. Reaction of Si2 and Si16 with N_3Ad (**Si17**) [17]

Similar to this Si16 can react with 1 equivalent of N_3Ad to give **Si17**. Si17 can also be obtained by reacting 2 equivalents of N_3Ad with Si2 (Scheme 14) [17]. ^1H NMR of Si16 appears at δ 5.88 ppm for backbone proton (NCH) and other are same as expected. ^{29}Si NMR resonance is at δ -34.34 ppm. It crystallises in triclinic space group *P*-1with two toluene in asymmetric unit. Also it has shorter N-N single bond (1.380(3) Å) and longer N-N double bond (1.257(3) Å). The CN bond distance is slightly shorter than unsubstituted NHC-derived triazene displaying better accepting properties of carbene carbon.



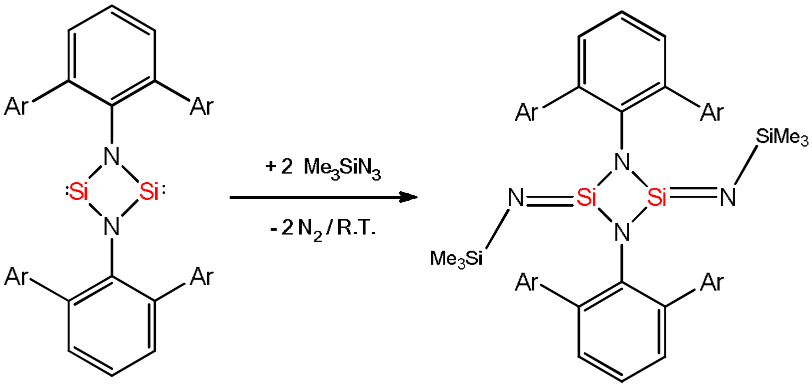
Scheme 15. Reaction of L^1SiCl_2 with arylazide (**Si18, Si19, Si20**) [18]

Silamines are compunds with polarised Si=N bond havi alkyl or aryl group on N for their stabilization. Roesky *et al.* in 2010, synthesised NHC-stabilized dichlorosilamines using aryl azides in toluene. Reaction of IPr.$SiCl_2$ (**Si2**) with bis(2,6-diisopropylphenyl)-carbodiimide affords NHC-stabilized dichlorosilaimine IPr.Cl_2Si=N(Diip) (**Si18**). Si2 reacts with an equimolar amount of 2,6-$Diip_2$-$C_6H_3N_3$ or 2,6-$Triip_2$-$C_6H_3N_3$ with clean formation of dichlorosilaimines IPr.Cl_2Si=N(2,6-$Diip_2$-C_6H_3) (**Si19**) and IPr.Cl_2Si=N(2,6-$Triip_2$-C_6H_3) (**Si20**), respectively (Scheme 15) [18]. All are yellow crystalline compuind with toluene in the lattice stable under inert atmosphere and are soluble in common organic solvents. ^{29}Si NMR resonance is at δ -107.07, -99.95, -99.70 ppm for Si18, Si19, Si20, respectively, shifted upfield w.r.t. Si2 due to higher coordinate silicon atom consistent to Si(IV) compounds. Si18 crystallises in monoclinic space group $P2_1/c$ with silicon having distorted tetrahedral geometry. Silaimine Si19 crystallizes in the monoclinic space group *C2/c*, whereas Si20 crystallizes in the triclinic space group P-1 with two molecules in the asymmetric unit. The silicon atom in each of Si19 and Si20 is four-coordinate, and exhibits a distorted tetrahedral geometry at silicon centre. The Si=N mean bond length for Si18, Si19, Si20 is 1.565(4) Å. The Si-C(carbene) bond distance is 1.917(5), 1.953(2) and 1.938(2) Å in Si18, Si19, Si20, respectively.



Scheme 16. Reduction of Si20 to make silaisonitrile (**Si21**) [20]

Organic nitriles and isonitriles are very stable but their silicon analogues are transient in low temperature argon matrix. After the reported synthesis of Si20, Ghadwal *et al.* in 2011, reported its reduction with KC$_8$ to make dimeric silaisonitrile, (ArNSi**:**)$_2$ (**Si21**) (where Ar = 2,6-bis(2,4,6-triisopropylphenyl)-phenyl). Since silicon resists multiple bonds, Si21 is supposed to be formed through [2+2] cycloaddition of monomeric silaisonitrile with elimination of two L^1 molecules (Scheme 16) [20]. It is isolated as yellow crystalline blocks with 21% yield.



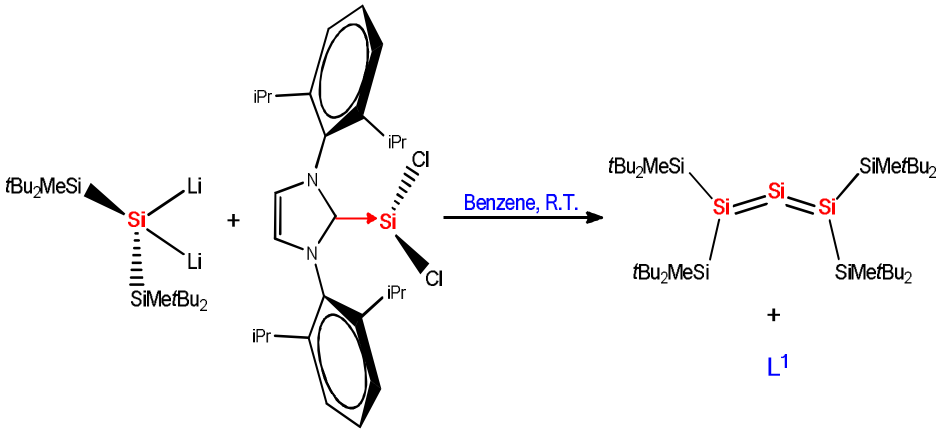
Si22

Scheme 17. Reduction of Si21 to make bis(silaimine) (**Si22**) [20]

Si21 reacts with trimethylsilyl azide (Me_3SiN_3) to give the first bis(silaimine) with three coordinated silicon atoms with colourless crystalline solid in 62% yield (**Si22**) (Scheme 17) [20]. Si21 and Si22 are stable under inert atmosphere and are soluble in common organic solvents. The ^{29}Si NMR resonance of Si21 is highly desheilded at δ 183.29 ppm, may be due to the presence of two silylene moieties. The EI-MS shows molecular ion [M^+] peak at *m/z* 1046 and base ion [$(M-C_3H_7)^+$] peak at *m/z* 1003, supporting its dimeric nature. The ^{29}Si NMR spectrum of Si22 are at δ -2.76 (trimethylsilyl; $SiMe_3$) and – 56.82 ppm (silaimine; ArNSi=N) which are slightly downfield may be due to silicon's lower coordination number.

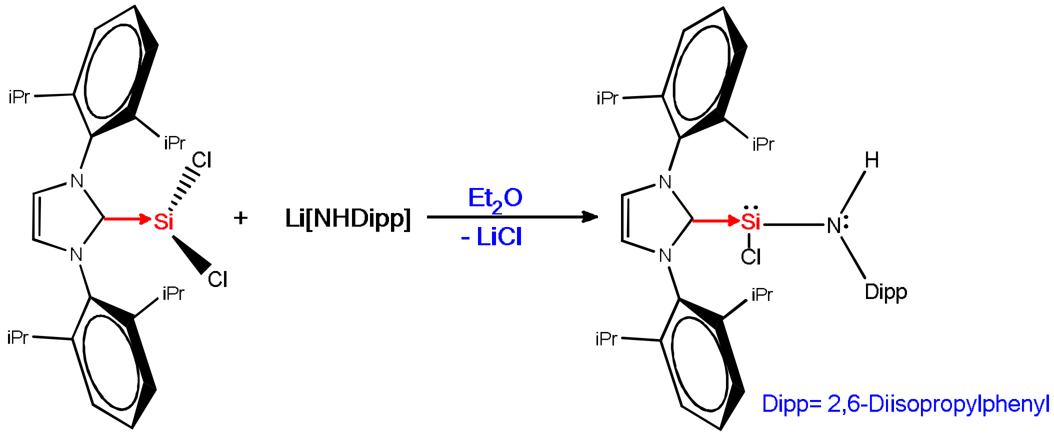
Si21 crystallises in the monoclinic space group *C*2/*c* in benzene. The asymmetric unit contains half a molecule of Si21 and one & a half molecule of benzene. Each silicon atom is two coordinate (first example of *base-free disilylene*). The Si2N2 ring is planar and the average Si-N bond distance is 1.755(1) Å. Si22 crystallises in the triclinic space group $P\bar{1}$ in toluene with half a molecule of Si22 and one & a half molecule of toluene in asymmetric unit. Each silicon atom is three coordinate (first example of *base-free bis(silaimine)*). The average Si-N bond distance is 1.724(2) Å which is slightly shorter than Si21. The exocyclic Si=N bond length is 1.564(2) Å.

The silicon analogues of allenes (trisilaallene) are very rare and unstable. They have a flexible Si=Si=Si skeleton which is bent. This bent is explained by Jahn-Teller distortion linked with the effective mixing of π and σ* orbital. The fist isolable tetrasilyl-substituted trisilaallene, viz, 1,1,3,3-tetrakis(di-tert-butylmethylsilyl)trisilaallene (**Si23**), was synthesised by Sekiguchi *et al.* in 2011. It's synthesis involves reaction of the dilithiosilane $(tBu_2MeSi)_2SiLi_2$ with the dichlorosilylene-NHC complex **Si2** in benzene at room temperature (Scheme 18) [21]. It is isolated as an air and moisture sensitive red solid with 40% yield by silica gel column chromatography with hexane in glove box in argon environment. Yeild of the product depends on the solvent and it decreases in polar solvents (*eg*. THF, ether).



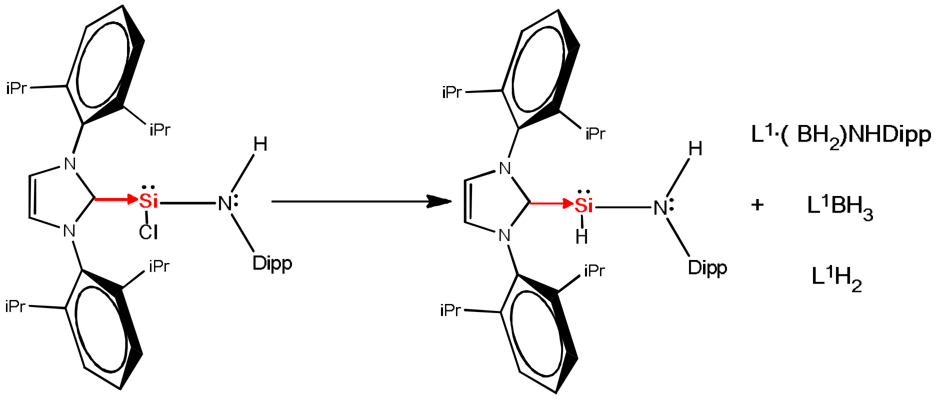
Scheme 18. Reaction of Si2 with dilithosilane to make trisilaallene (**Si23**) [21]

^{1}H NMR of Si23 shows only two peaks of -Me and -*t*Bu group of *t*Bu$_2$MeSi substituent. ^{29}Si NMR of Si23 displays three resonance at δ 22.4, 44.6, and 418.5 ppm of the substituent silicon atoms (*t*Bu$_2$MeSi), terminal silicon atoms (Si=Si=Si), and central silicon atom (Si=Si=Si), respectively. The UV_vis absorption spectrum of Si23 in hexane exhibits an absorption band at 400 nm (ε 3400 M^{-1}cm^{-1}) showing a π-π* transition. Theoretical calculation shows that the central bend angle is 164.3° which is larger than the un-substituted trisilaallene. This is due to the electronic effect of the silyl substituents and the steric effect by four bulky *t*Bu$_2$MeSi groups. The Si=Si bond distances are 2.1792 and 2.1742 Å. The terminal silicon of Si=Si=Si are slightly pyramidalized *i.e.*, they are not planar. Also, it undergoes thermal isomerisation to thermodynamically more stable cyclotrisilene (orange-red crystals) at higher temperature.



Scheme 19. Reaction of Si2 with Li[NHDipp] to make Si(II)amidohalide (**Si24**) [26]

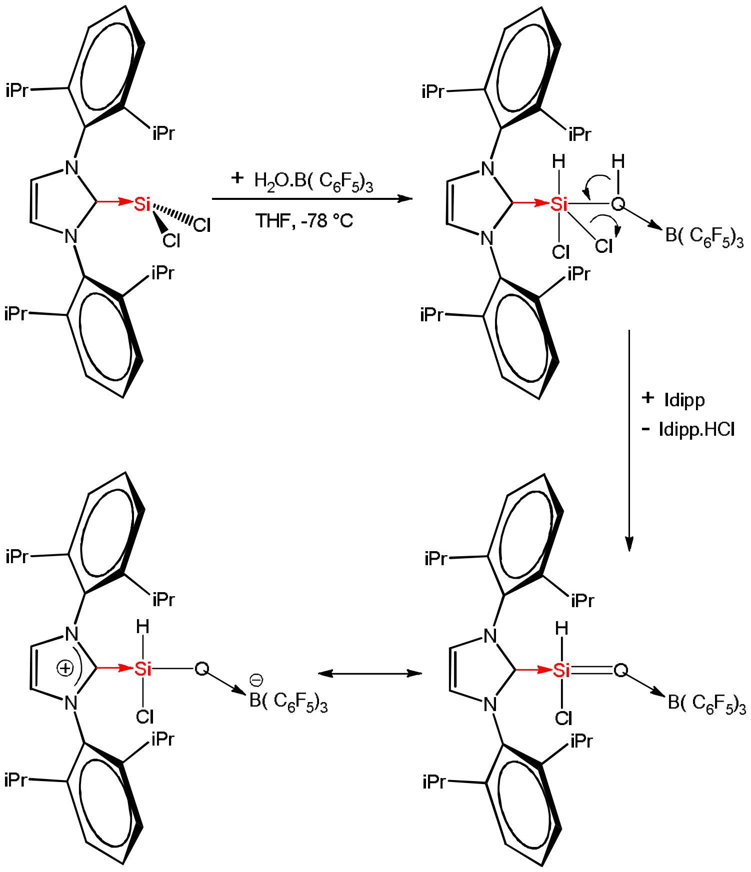
In 2012, Rivard *et al.*, prepared N-heterocyclic carbene stabilized amidohydride complexes of the general form L^1·EHNHDipp (E= Si, Ge, or Sn). The silicon analougue of this amidohydride was synthesised with the Si(II) amidohalide precursor (L^1·SiClNHDipp) (**Si24**). The precursor is prepared by treating Si2 with one equivalent od Li[NHDipp] in ethyl ether (Et_2O) (Scheme 19) [26]. Si24 is isolated as yellow air and moisture sensitive solid, stable at ambient temperature, in 45% yield. ^{1}H NMR of Si24 shows N-H peak at δ 4.14 ppm. ^{29}Si NMR resonates at δ -6.0 ppm which is upfield w.r.t. Si2. IR stretching frequency of N-H residue is found in the narrow range of 3357-3371 cm^{-1}. X-ray crystallographic studies tells that, Si24 has distorted trigonal pyramidal geometry at the 3-coordinate silicon centre. Si-Cl is oriented towards L^1 ligand. The Si-$C_{carbene}$ bond distance is 1.980(3) Å. The Si-N bond length is 1.765(2) Å which is slightly longer than the Si-N bond of Roesky dimeric silaisonitrile (Si21).



Scheme 20. Reaction of Si24 with Li[BH_4] to make Si(II)amidohydride (**Si25**) [26]

Si24 on reaction with one equivalent of Li[BH_4] in Et_2O gives mixture of L^1·SiH(BH_3)NHDipp (**Si25**), L^1·(BH_2)NHDipp, L^1BH_3 and L^1H_2 (Scheme 20) [26]. Si25 was isolated in pure form (34% yield) by cooling a saturated solution of the crude product mixture in Et2O/hexanes to -35 °C. ^{1}H NMR of Si25 shows broad SiH resonance with resolvable flanking ^{29}Si satellites ($^1J_{SiH}$=160.3 Hz), located at δ 5.13 ppm. The proximal amide proton in the -NHDipp group was detected as a doublet resonance at δ 1.94 ppm ($^3J_{HH}$=5.5 Hz), with the observed pattern resulting from the coupling of an NH hydrogen atom with the adjacent silicon-bound hydride. Coordinated BH_3 in Si25 was confirmed by ^{11}B NMR showing a quartet resonance at δ -44.1 ppm with an expected coupling constant of $^1J_{BH}$=89.5 Hz. IR spectrum shows an absorption band at 3559 cm^{-1} of N-H stretching vibration, a broadened $^{10/11}$B-H stretching modes from 2326 to 2237 cm^{-1}, and a sharp Si-H stretching band at 2096 cm^{-1}.

Formyl chloride is a very reactive and useful reagent used in several organic reactions for formylation. Its silicon analogue is much more challenging to synthesise. In 2012, Ghadwal *et al.*, synthesied the first stable silacarbonyl compound, as well as the first silacarbonyl halide, Idipp.SiH(Cl)=O.B(C_6F_5)$_3$ (**Si26**). They reacted **Si2** with H_2O.B(C_6F_5)$_3$ in presebce of L^1 (Idipp) for removing HCl (Scheme 21) [27]. **Si26** was obtained from a toluene solution with 26% yield as colourless crystals. It is soluble in common organic solvents and is stable in inert atmosphere for a fairly good time. There is a significant double bond character between Si & O atom in **Si26** and have a resonating form as well.

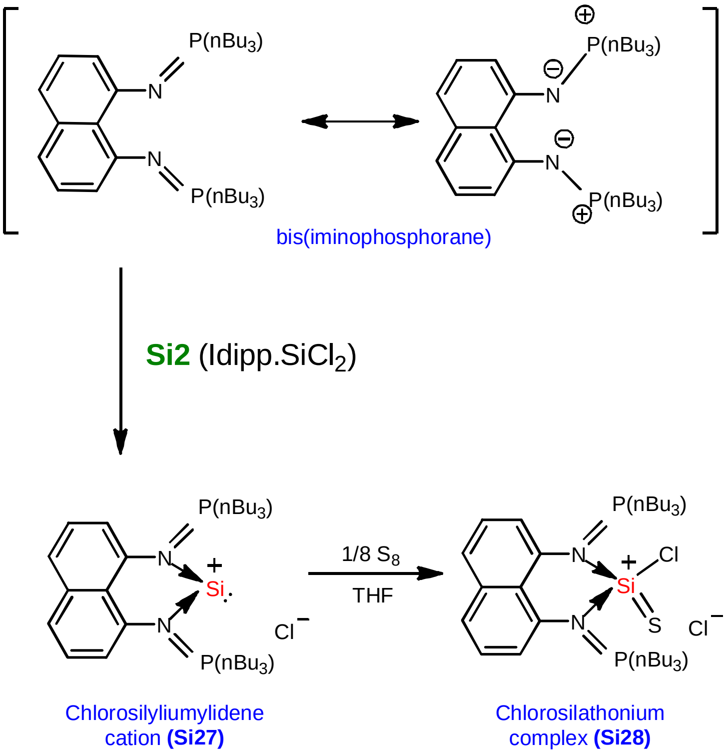


Scheme 21. Reaction of Si2 to make silaformyl chloride (**Si26**) [27]

A broad resonance ^{1}H NMR of Si-H proton was obtained at δ 5.55 ppm. The ^{29}Si{^{1}H} NMR spectrum is obtained as a singlet at δ -49.78 ppm. It crystallizes in monoclinic space group *P*2(1)/*c* with two molecule in asymmetric unit. The silicon centre is tetrahedrally coordinated. The Si-O bond distance is 1.568(15) Å which is smaller than Si-O single bond length (1.64 Å) and larger than the Si-O double bond length (1.53 Å). The Si-Cl and Si-$C_{carbene}$ bond distances are 2.049(8) Å and 1.911(2) Å, respectively, which are shorter than **Si2**.

Divalent silicon cations (silyliumylidene cation; [RSi:]$^+$; R = H, halogens, organo groups) are very hard to make. They are stabilized using bulky monovalent substituents. [ClSi:]$^+$, monochlorosilyliumylidene cation is a very good silyliumylidene precursor as the Cl is suitably replaced by nucleophile. They are very unstable and are found in gas phase. In this field, Driess *et al.*, in 2012, synthesized the first isolable chlorosilyliumylidene species (**Si27**) stabilized by bis chelating agent, bis(iminophosphane) by reacting equimolar **Si2** at room temperature with it

(Scheme 22) [28]. **Si27** is obtained as colourless crystals in THF and dichloromethane at -20° C with 46% yield.It is air and moisture sensitive but stable in solid state in dry and inert atmosphere. It is insoluble in toluene and sparingly soluble in THF, pointing it to be a salt.

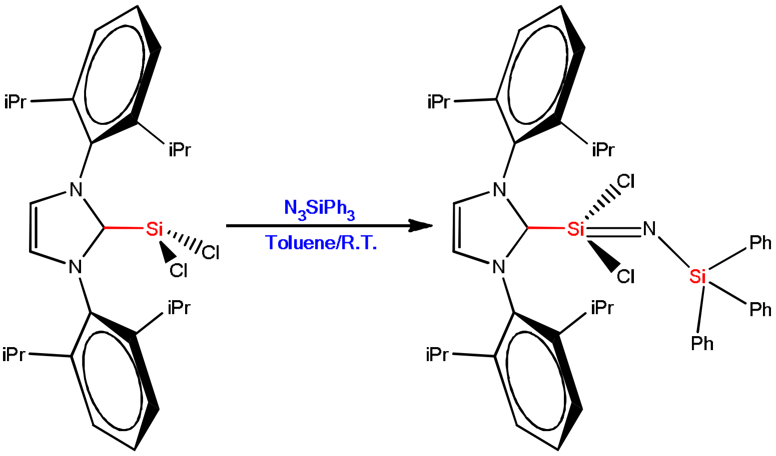


Scheme 22. Reaction of Si2 to make chlorosilyliumylidene chroride and chlorosilathonium complex (**Si27** & **Si28**) [28]

It crystalizes in monoclinic space group $P2_1/n$. The silicon centre is tricoordinated with one Cl and two N of chelating agent. The other anionic chlorine is situated far away at the smallest distance of 6.704 Å. A six-membered ring made by C_3N_2Si. Silicon lies out of the plane made by C_3N_2, by 38°. The Si-Cl bond distance is 2.172(2) Å which is similar to **Si2**. The two Si-N bond distances are also similar with magnitude of 1.874(3) Å and 1.835(3) Å. The average P-N distance is 1.6625 Å which lies between the P-N single and double bond lengths. The ^{31}P NMR spectrum shows it is downfield shifted at δ 57.7 ppm than the precursor at δ 11 ppm in [D_2]dichloromethane. A triplet at δ -3.3 ppm ($^{2}J(Si,P)$= 22.3 Hz) was seen for $^{29}Si\{^{1}H\}$ NMR spectrum.

Si27 on further adding elemental sulphur gave remarkable chlorosilathionium complex (**Si28**) (Scheme 22) [28]. It is isolated as colourless crystals in 81% yield. It crystallizes in triclinic space group $P1$, with two independent molecule in asymmetric unit. The ^{31}P NMR spectrum of **Si28** is downfield shifted than **Si27** at δ 66 ppm. It shows a triplet at δ -26.7 ppm ($^{2}J(Si,P)$= 9.4 Hz) for ^{29}Si NMR which is upfield shifted than **Si27**. The six-membered C_3N_2Si ring is more wrinkled with dihedral angle of 49.6° and 49.3° between C_3N_2 and N_2Si atoms than **Si27**. The increased coordination number in **Si28**(+IV) from **Si27**(+II) gives shortened Si-Cl and Si-N bond lengths of 2.087(2) Å and 1.785 Å respectively. The Si=S bond distances are 1.984(2) Å and 1.977(2) Å. **Si28** acts as a potentially strong Lewis acid catalyst in organic transformations because of stability(exists in several resonating forms) and ylide nature of P=N and Si=S.

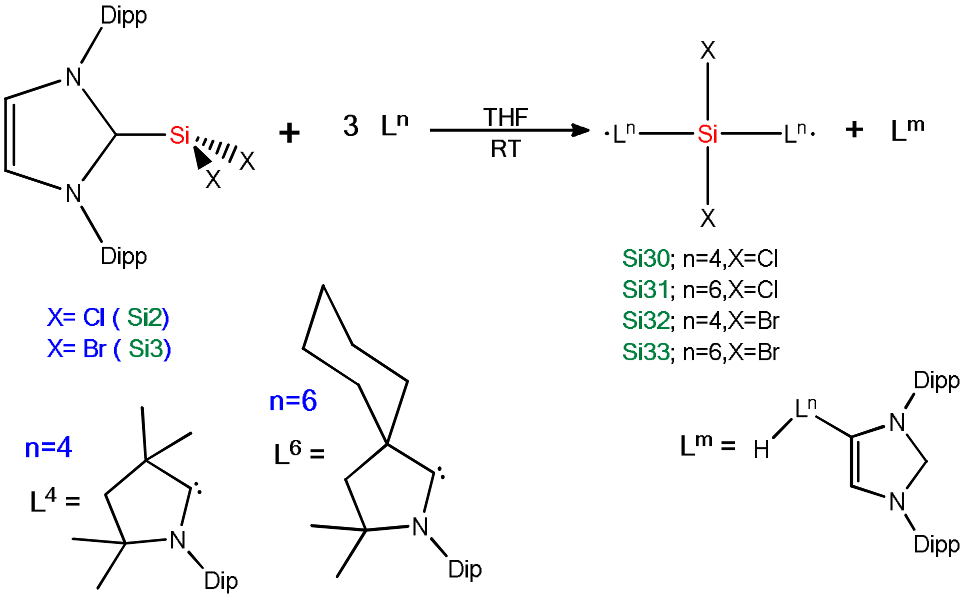
Vinylsilanes are important compounds used as synthetic intermediates, monomer in copolymer plastics and coupling agents. They are generally synthesized by the transition metal catalysed hydrosilylation and bis-silylation of alkynes. Cui *et al.* in 2012, showed a bis-silylation reaction of alkynes without using any transition metal catalyst with the help of NHC-stabilised silylaminosilylene (**Si7**). The reaction is highly stereospecific and proceeds via 1,4-silyl migration from the silylamino nitrogen atom to one of the alkyne central carbon atom.



Scheme 23. Reaction of **Si2** to make silaimine (**Si29**) [31]

Ghadwal *et al.* in 2012, synthesised another NHC stabilized silaimines. For this, they reacted **Si2** with equimolar triphenylsilyl azide to yield **Si29** (Scheme 23) [31]. **Si29** is soluble in toluene, benzene and THF. The ^{29}Si NMR spectrum shows two peaks at δ -29.64 ppm for $SiPh_3$ and δ -75.25 ppm for $SiCl_2$. It crystallizes in monoclinic space group $P2_1/c$ with four-coordinated silicon centre showing distorted tetrahedral geometry. The average Si-Cl bond distance is 2.0745(11) Å and the Si-$C_{carbene}$ bond distance is 1.924(3) Å which are both shorter than **Si2**. The Si-N bond length is 1.581(2) Å.

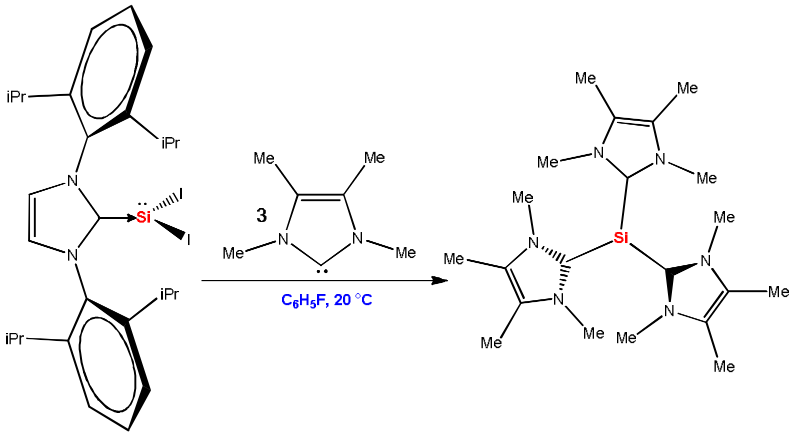
Radicals and biradicals are the important chemical species of many reactions and processes. But their isolation and characterisation is very difficult. Roeskt *et al.* in 2013, developed a notable synthetic pathway for air-stable 1,3-biradicals $(L\cdot)_2SiX_2$ (X=Cl,Br) using $L^1.SiCl_2$ and cAAC (cyclic alkyl(amino) carbene).



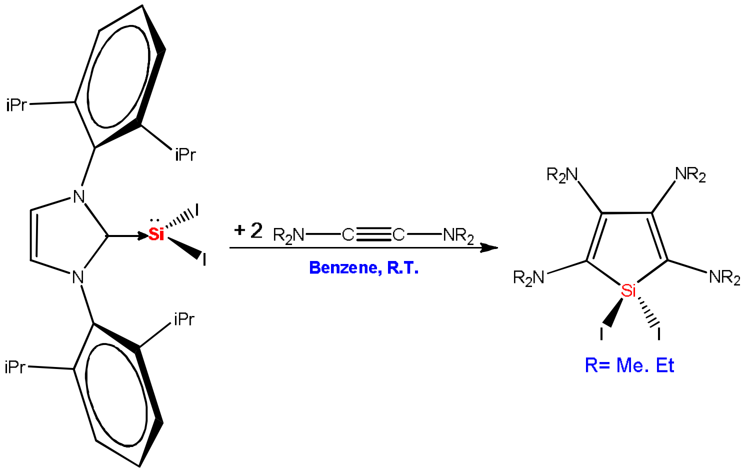
Scheme 24. Synthesis of biradical (**Si30** to **Si33**) [34]

Si30, **Si31**, **Si32** and **Si33** are synthesised by reacting L^1-SiX_2 with three equivalents of the required cAAC in THF at room temperature (Scheme 24) [34]. Coupled NHC (L^m) are obtained as the by-product. The percentage yield of **Si30** and **Si31** depends on the ratio of L^1-SiX_2 and cAAC. The can be crystallised from n-hexane or THF. **Si30** crystals do not contain any lattice solvent but **Si31** contains n-hexane or THF as lattice solvent. **Si31** are obtained as blue plates stable upto a week in air like **Si30**. **Si32** is isolated as microcrystalline solid which is stable in an inert atmosphere showing its instability. **Si33** is isolated as large blue blocks in 6% yield. Thus, the stability of these biradicals formed depends on the nature of X (Cl, Br) on the silicon centre (more electronegative leads to more stability). The ^{29}Si NMR spectrum is silent for all. The absorption spectrum shows a maxima ranging from 565 to 585 nm for all. **Si30** crystallises in monoclinic space group $C2/c$ with silicon in distorted tetrahedral geometry. The Si-$C_{carbene}$ bond distance is 1.8455(16)/1.8482(17) Å. **Si31** and **Si33** are isostructural and crystallises in monoclinic space group $P2_1/n$ with half *n*-hexane in asymmetric unit. The Si-Ccarbene bond distances in **Si31**.0.5 *n*-hexane is 1.854(2)/1.8585(18) Å and in **Si33**.0.5 *n*-hexane is 1.843(2)/1.8497(18) Å.

NHC-stabilized iodosilylenes are very reactive as they have the iodide group present which serves as a good leaving group and undergoes displacement reaction to give cationic silicon(II) species. This was first demonstrated by Filippou *et al.* in 2013. They added 1,3,4,5- tetramethyl-imidazole-2-ylidene (IMe_4) to L^1SiI_2 (**Si9**) in fluorobenzene (Scheme 25) [35]. This readily gave $[Si(IMe_4)_3]^{2+}I^-$ (**Si34**) as `precipitate in 79% yield. It is a light yellow powder which is soluble in CH_2Cl_2. The dication $[Si(IMe_4)_3]^{2+}$, has C_3 symmetry with propeller like pyramidal structure. The nearest Si-I distance is 5.85 Å. The positive charge on silicon centre is delocalized on the three imidazole rings making the Si-C$_{carbene}$ bond distance to be 1.915(3) Å. The ^{29}Si{^{1}H} NMR spectrum in CD_2Cl_2 displays a strongly shielded ^{29}Si NMR peak at δ -89.9 ppm. The ^{13}C{^{1}H} NMR spectrum shows unique C$_{carbene}$ signal at δ 150.7 ppm.



Scheme 25. Reaction of L^1SiI_2 to make cationic silicon(II) compound (**Si34**) [35]

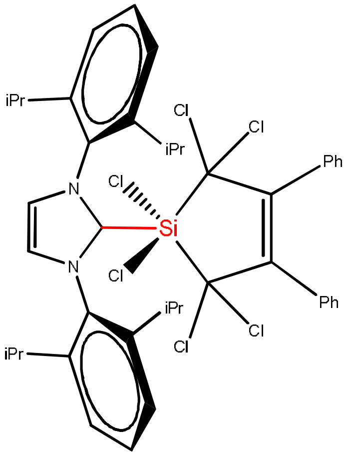
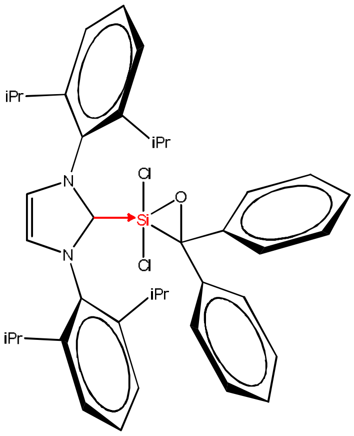
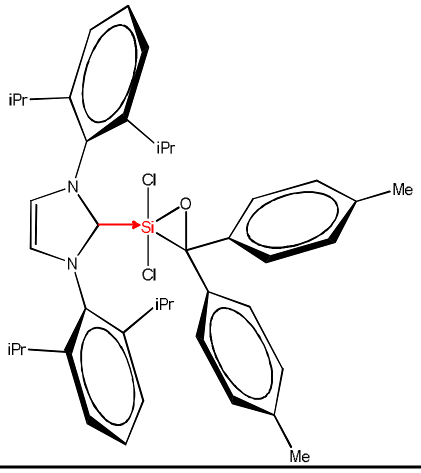


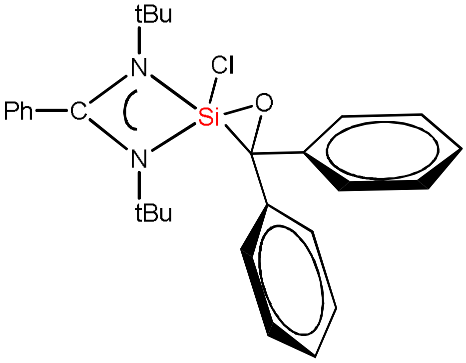
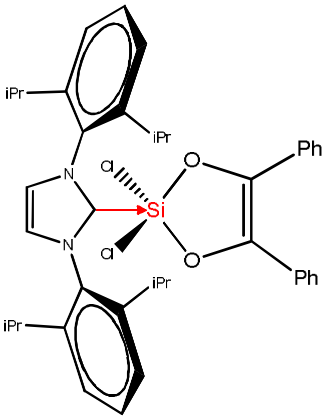
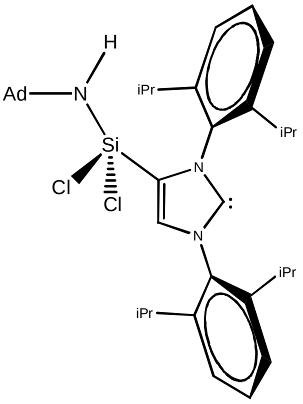
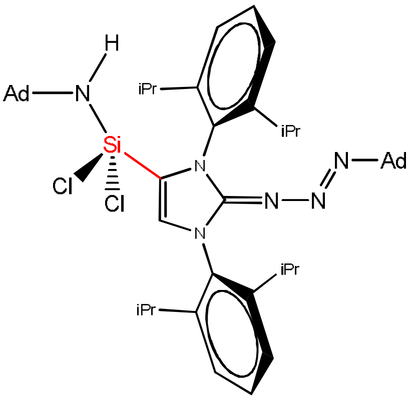
Scheme 26. Reaction of L^1SiI_2 to make tetra(dialkylamino)-1-H-silole (**Si35** & **Si36**) [37]

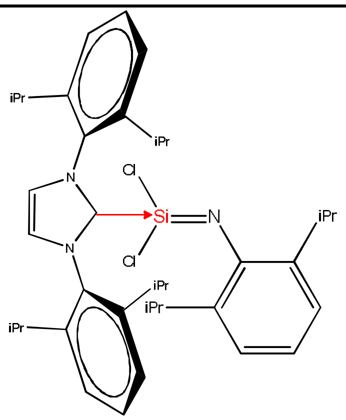
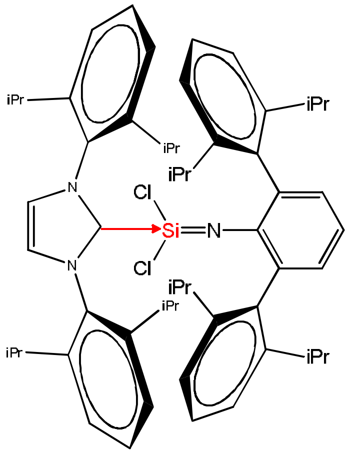
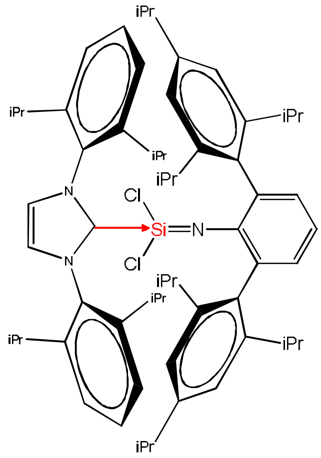
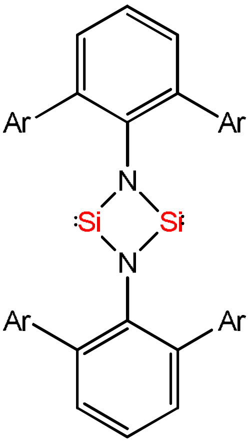
Using this same property of L^1SiI_2, Filippou *et al.* in 2014 synthesised the silicon containing five membered ring. For this they added two equivalents of bis(dialkylamino)acetylene (R_2N-C≡C-NR_2) to L^1SiI_2 (**Si9**) in benzene (Scheme 26) [37]. This yields tetra(dialkylamino)-1-H-silole, $SiI_2(C_4(NR_2)_4)$, where R can be methyl (**Si35**) or ethyl (**Si36**). Both are isolated as orange, water sensitive crystals in *n*-hexane at -60° C (**Si35**) and -30° C (**Si35**). **Si35** decomposes to a black mass at 111° C and **Si36** melts at 85° C without decomposition. They are the [2+2+1] cycloaddition product, feasible because of the high nucleophilicity of the ynediamines (R_2N-C≡C-NR_2). The Si-C bond distances are between 1.827(11)-1.854(2) Å. The Si-I bond distance is 2.463 Å in **Si35** and 2.466 Å in **Si36**. All the amino groups are rotated out of the ring resulting in minimum steric repulsion. The C$_{ring}$-N bond lengths are between 1.39-1.43 Å (close to C_{sp^2}-N_{sp^3}). ^{1}H and ^{13}C NMR spectrum displays single set of resonance for N-alkyl substituents and hence it confirms the rapid rotation of amino groups. The ^{29}Si NMR spectrum shows peak at δ -87.8 ppm for **Si35** and δ -83.5 ppm for **Si36** in C_6D_6.

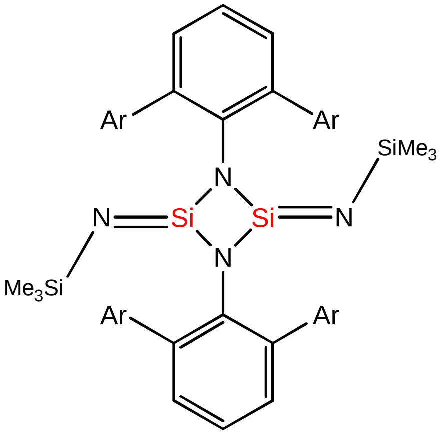
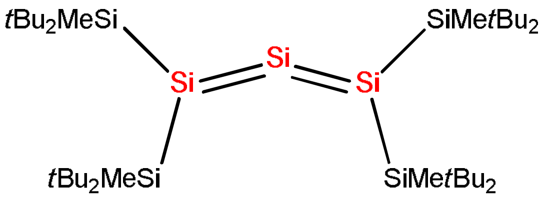
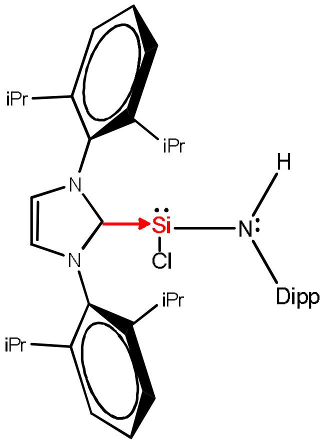
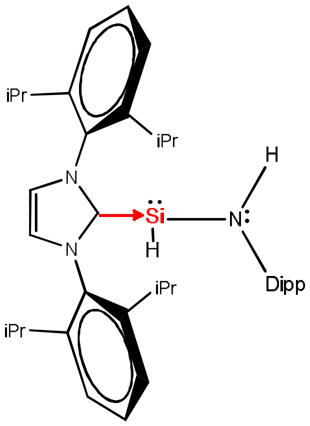
Table 2

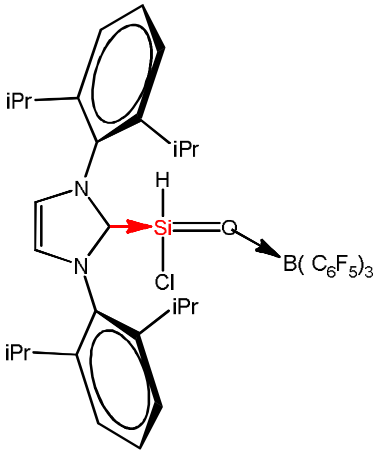
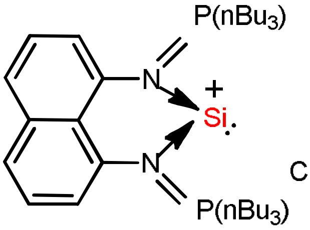
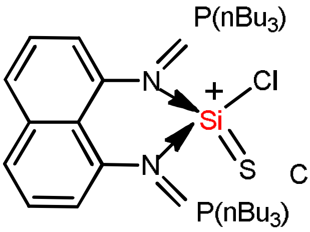
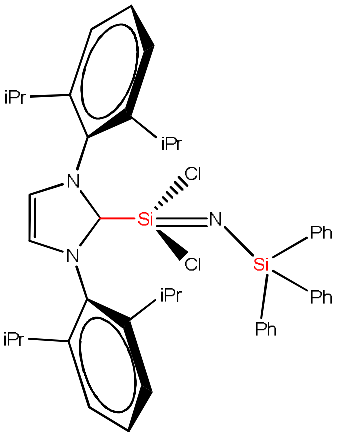
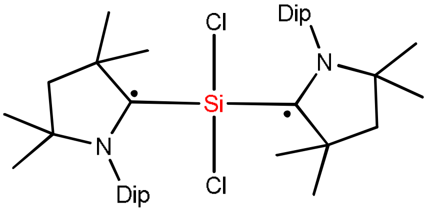
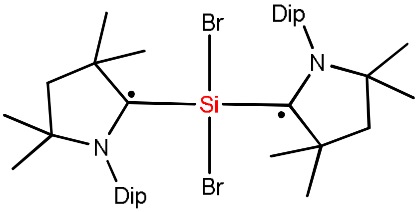
Key features of structurally characterized molecules consist of C_{NHC} Si bond (after reaction)

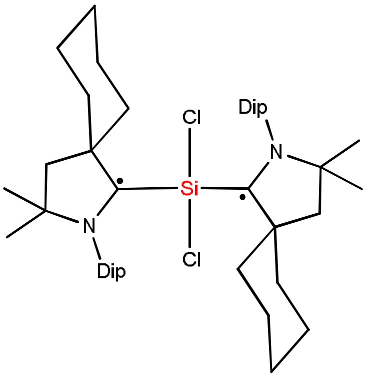
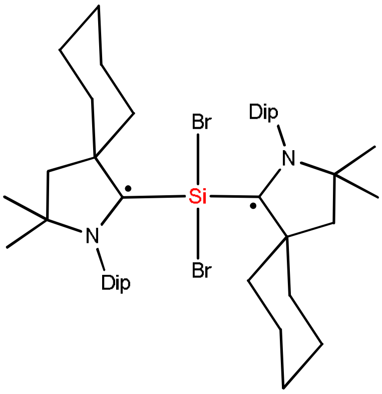
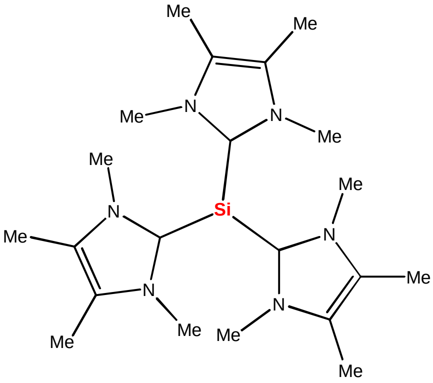
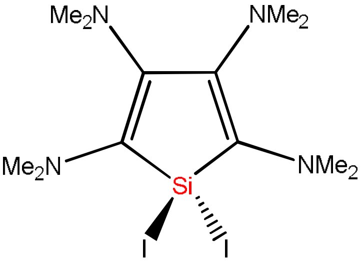
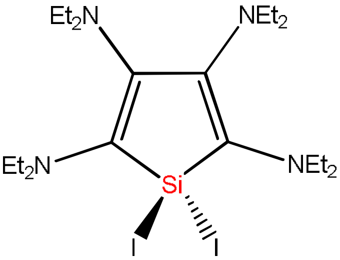
Molecule	Compound No.	^{13}C NMR of NCN, δ ppm	^{29}Si NMR of C-Si, δ ppm	C-Si separation, Å	Reference
	(Si11)	Unknown	-2.84 & -142.47	1.911(17)	[9]
	(Si12)	Unknown	-123.85	1.9653(15)	[13]
	(Si13)	Unknown	-123.39	1.9724(17)	[13]

	(Si14)	Not present	-115.53	Not present	[13]
	(Si15)	Unknown	-99.50	1.939(2)	[13]
	(Si16)	224.21	-30.01	Not present	[17]
	(Si17)	unknown	-34.34	Not present	[17]

	(Si18)	unknown	-107.07	1.917(5)	[18]
	(Si19)	unknown	-99.95	1.953(2)	[18]
	(Si20)	unknown	-99.70	1.938(2)	[18]
 **Ar= 2,6-bis(2,4,6-triisopropylphenyl)-phenyl**	(Si21)	Not present	Not present	Not present	[20]

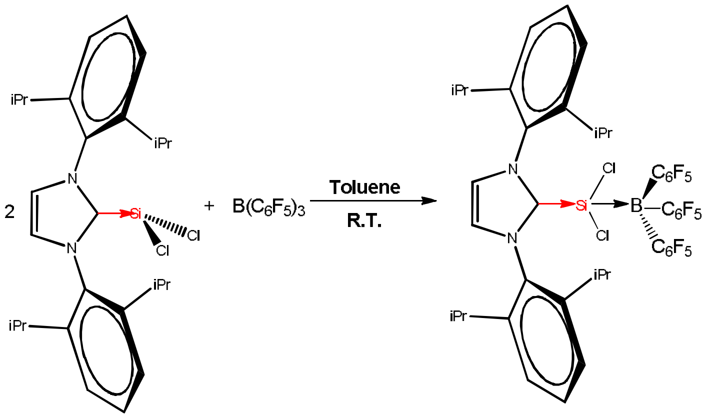
 **Ar= 2,6-bis(2,4,6-triisopropylphenyl)-phenyl**	(Si22)	Not present	Not present	Not present	[20]
	(Si23)	Not present	Not present	Not present	[21]
 **(Dipp = 2,6-Diisopropylphenyl)**	(Si24)	Unknown	-6.0	1.980(3)	[26]
 **(Dipp = 2,6-Diisopropylphenyl)**	(Si25)	unknown	Unknown	1.9431(15)	[26]

	(Si26)	unknown	-49.78	1.911(2)	[27]
	(Si27)	Not present	Not present	Not present	[28]
	(Si28)	Not present	Not present	Not present	[28]
	(Si29)	unknown	-75.25	1.924(3)	[31]
	(Si30)	unknown	Silent	1.8455(16) / 1.8482(17)	[34]
	(Si31)	unknown	Silent	unknown	[34]

	(Si32)	unknown	Silent	1.854(2)/ 1.8585(18)	[34]
	(Si33)	unknown	Silent	1.843(2)/ 1.8497(18)	[34]
	(Si34)	150.7	-89.9	1.915(3)	[35]
	(Si35)	Not present	Not present	Not present	[37]
	(Si36)	Not present	Not present	Not present	[37]

3.3 Reaction of NHC:SiX_2 (X = Cl,Br,I,R) with Main Group Substrates

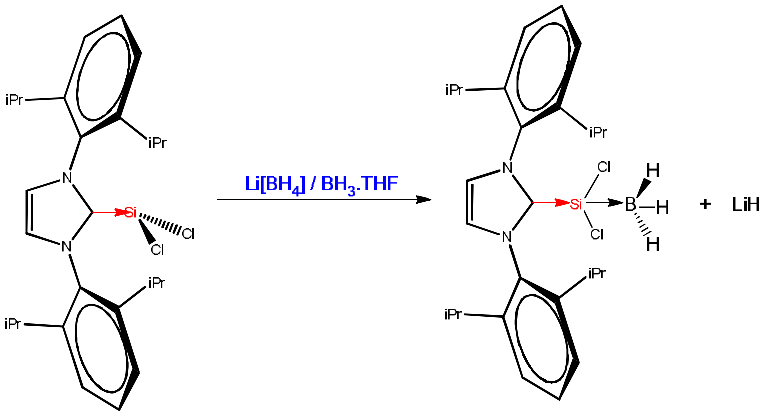
Dihalosilylenes are ambiphilic in nature *i.e.* they can acts as Lewis acid as well as Lewis base. Si2 is a σ- donor ligand having a steriochemically active lone pair at silicon. So, it can act as Lewis base. Using this Roesky *et al.* in 2010 synthesised a N-heterocyclicsilylene-borane adduct. The reaction of L^1SiCl_2 (**Si2**) with $B(C_6F_5)_3$ in toluene gave L1→SiCl2→$B(C_6F_5)_3$ (**Si37**) on storage at -35 °C for two days (Scheme 27) [11]. The reaction is unsuccessful with $B(OPh)_3$ and $BF_3.Et_2O$.



Scheme 27. Reaction of L^1SiCl_2 as Lewis Base (**Si37**)[11]

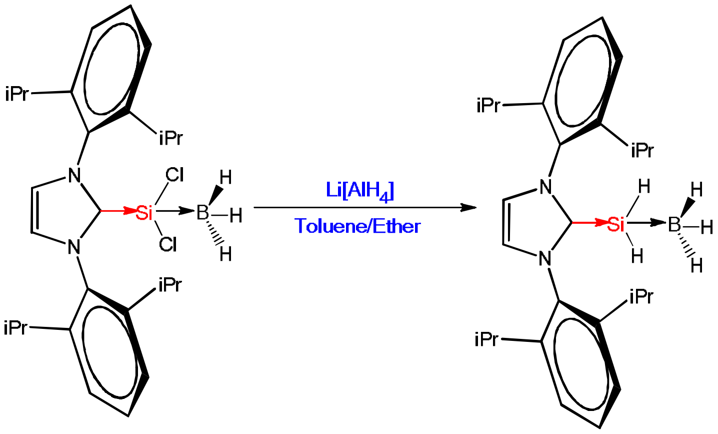
Si37 is crystallized as colourless crystals, is soluble in common organic solvents and is stable in inert gas atmosphere. The ^1H NMR exhibits resonance for the NHC ligand (δ = 0.80 ($CHMe_2$), 1.15 ($CHMe_2$), 2.62 ($CHMe_2$), 6.29 (NCH), 6.89 (m-C_6H_3), 7.02–7.07 ppm (p-C_6H_3)) with upfield shifted resonances relative to Si2. The ^{11}B NMR shows broad resonace agreeing to four-coordinate Boron atom. The ^{19}F NMR spectrum lies in expected region. And the ^{29}Si NMR is shifted to higher field at δ -53.19 ppm than Si2. It crystallises in triclinic space group $P\bar{1}$ as a twin with toluene molucules in crystal lattice. Both silicon and boron are four coordinated with distorted tetrahedral geometry. The $C_{carbene}$-Si bond length is 1.965(5) Å and average Si-Cl bond length is 2.06195(19) Å which are both shorter than Si2. Si-B bond distance is 2.1135(6) Å. There are two bonding modes present, first is C→Si (σ acceptor Si) and second, Si→B (σ donor Si) which was justified by the computational studies. Also, this showed that the two C→Si and Si→B donor bonds are qualitatively different from respective single bonds. The C→Si bond is very polar indicating hard NHC donor ligand and covalent Si→B bonds confirms silylene as much softer ligand.

Silicon(II) dihydrides are very difficult to make and exists as intermediate in many reactions like hydrosilane polymerisation and in synthesis of halomethylsilanes. In 2011, Roesky *et at.*, tried to synthesise it by reacting **Si2** with equivalent amount of $Li[BH_4]$ or BH_3.THF solution. Rather than giving hydride, it gave the chlorosilylene-BH$_3$ adduct (**Si38**) ($L_1SiCl_2{\rightarrow}BH_3$) with elimination of LiH (Scheme 28) [19].



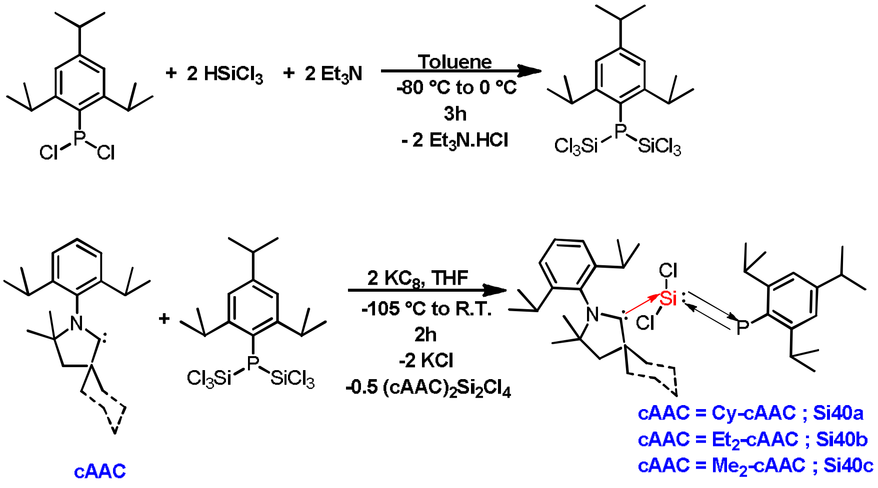
Scheme 28. Synthesis of $L^1SiCl_2.BH_3$ adduct (**Si38**)[19]

Si38 is stable in both solution and solid atate in room temperature under inert gas atmosphere. The ^{29}Si NMR shows a quartet at δ 30.72 ppm because of ^{11}B (I= 3/2) quadrupolar nucleus. The ^{11}B NMR also shows a quartet at δ -38.78 ppm displaying the coupling of hydrogen atom to the boron atom with intensity 1:3:3:1. Similarly, ^{1}H NMR spectrum shows a resonance at δ -1.02 to +0.40 ppm with an intensity of 1:1:1:1, indicating the coupling of the hydrogen nuclei with the quadrupolar ^{11}B nucleus. The IR spectrum shows $\nu_{B\text{-}H}$ vibrational bands at 2356 and 2320 cm^{-1}. **Si38** adduct crystallizes in monoclinic space group $P2_1/n$ with four-coordinated silicon and boron centres in distorted tetrahedral geometry. The Si-B bond length is 1.965(2) Å which is shorter than in **Si37**. The Si-Ccarbene bond distance is 1.937(2) Å and the average Si-Cl bond distance is 2.0839(7) Å which are both shorter than **Si2**.



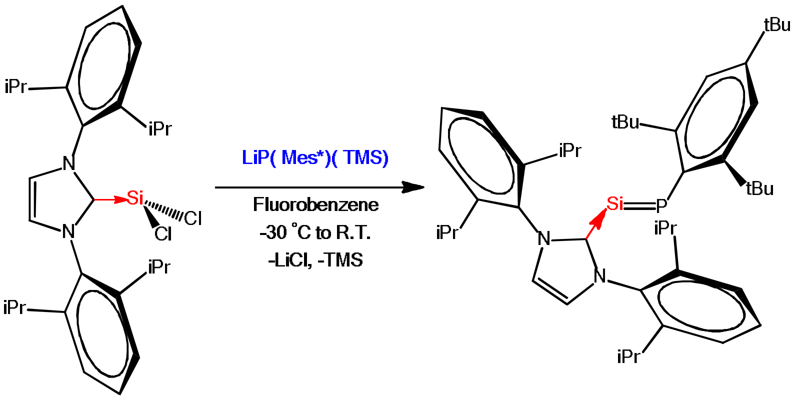
Scheme 29. Synthesis of $L^1SiH_2.BH_3$ adduct (**Si39**)[29]

Further Rivard *et al.* in 2012, reduced **Si38** using LiAlH$_4$ in low polarity solvent mixture (toluene/ether) for 1.5 hours. This yielded 55% of Si(II) dihydride adduct ($L^1.SiH_2.BH_3$) (**Si39**) as colourless solid (Scheme 29) [29]. The C$_{carbene}$-Si bond distance is 1.9284(15) Å and the Si-B bond distance is 1.992(2) Å. IR spectrum shows a sharp band at 2096 cm^{-1} because of fused ν_{sym} and ν_{asym} Si-H stretching mode and $\nu_{B\text{-}H}$ stretching vibrations in a range of 2238 to 2345 cm^{-1}. The ^{29}Si{^{1}H} and ^{11}B NMR spectrum are obtained as a quartet at δ -55.6 ppm ($^{1}J_{Si\text{-}B}$ = 46 Hz) and δ -46.2 ppm ($^{1}J_{B\text{-}H}$ = 93 Hz), respectively.



Scheme 30: Synthesis of carbene→SiCl2→P−Ar (**Si40**)[38]

The unstable species dichlorosilylene was previously stabilized by carbene. The lone pair of electrons on the silicon atom of (carbene)SiCl$_2$ can form a coordinate bond with electron deficient elements. Also, as demonstrated by Roesky *et al.*, cAAC analogue of NHC-SiCl$_2$ possesses singlet diradical character and therefore are isolated in dimeric form. cAAC are stronger σ donor and π acceptor than NHC and can also stabilize many main group elments rare compounds like hosphasilenes. Stalke *et al.* in 2015 used these facts to stabilize a phosphinidene (Ar−P, an easy access to the precursor Ar-P(SiCl$_3$)$_2$) and synthesis and characterisation of carbene-diclorosilylene stabilized phosphinidene with the general formula carbene→SiCl$_2$→P−Tip (Tip = 2,4,6-triisopropylphenyl) (Scheme 30)[38]. The reaction of Tip-P(SiCl$_3$)$_2$ with cAAC and KC$_8$ in 1:2:2 molar ratioin THFgave cAAC→SiCl$_2$→P-Tip (**Si40**) at -105° C {cAAC= Cy-cAAC (**Si40a**), Et$_2$-cAAC (**Si40b**), Me$_2$-cAAC(**Si40c**)}. It was obtained as dark blue blocks from *n*-hexane in 45-50% yield. They are stable for months at 0° C in inert atmosphere. If cAAC is replaced by NHC, the colour of the crystals changes to dark red. It decomposes after 170° C (**Si40a**) and 165° C (**Si40b-c**). ^{29}Si NMR spectrum shows a doublet at δ -6.56 ppm ($^{1}J_{Si\text{-}P}$ = 198.4 Hz) for **Si40a**, δ -7.48 ppm ($^{1}J_{Si\text{-}P}$ = 203.6 Hz) for **Si40b** and δ -7.89 ppm ($^{1}J_{Si\text{-}P}$ = 195.5 Hz) for **Si40c**. The ^{31}P NMR peaks for **Si40a/b/c** are -123.09/-122.30/-123.27 ppm, respectively. The ^{13}C NMR resonance was observed in a range of δ 208.05-211.44 ppm. **Si40a** crystallises in *Pbca* space group with distorted tetrahedral geometry at silicon atom. The Si-C$_{carbene}$ approximate bond distance is 1.84 Å.

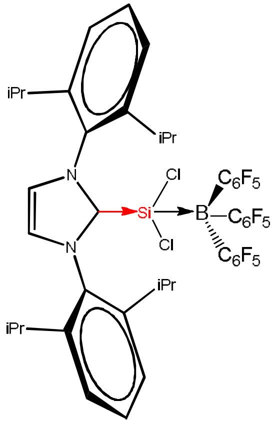


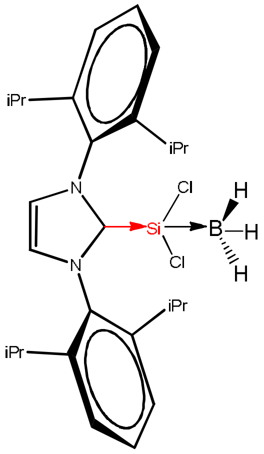
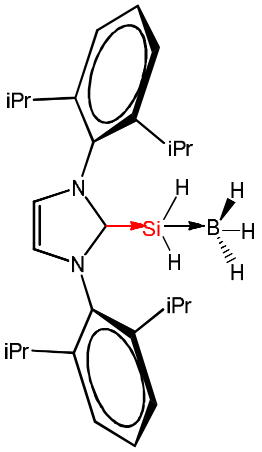
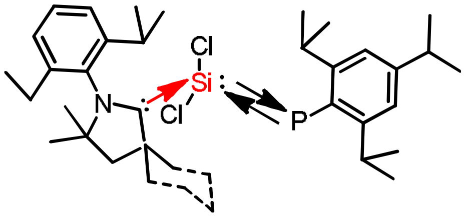
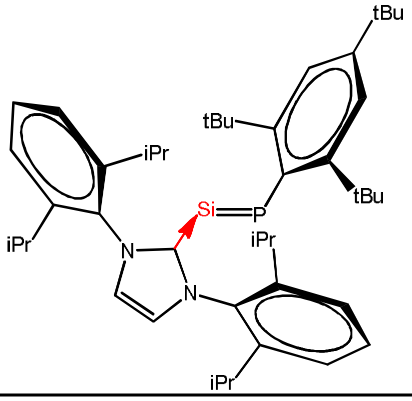
Scheme 31: Synthesis of NHC stabilized phosphasilenylidene (**Si41**)[39]

Earlier, the silylidynephosphanes were very difficult to make which features Si=P. Filippou *et al.* in 2015, synthesised stable NHC stabilized phosphasilenylidene (**Si41**). For this they added one equivalent of LiP(Mes*)(TMS) (Mes*=2,4,6- $t\text{Bu}_3\text{C}_6\text{H}_2$; TMS=SiMe_3) to **Si2** in fluorobenzene solution at -30° C (Scheme 31)[39]. The product formation is analysed by ^{31}P NMR. **Si41** is purified by fractional distillation in *n*-hexane as a bright orange air sensitive solid in 39% yield. The molecular structure **Si41**.Et_2O underwent single crystal XRD which reveals that silicon and phosphorus uses predominantly their *p*-orbital for S=P bond formation with the bond length of 2.1188(7) Å. The ^{29}Si{^{1}H} NMR spectrum of **Si41** in C_6D_6 displays a doublet signal at δ 267.3 ppm ($^{1}J_{(\text{P,Si})}$= 170.4 Hz). The ^{31}P{^{1}H} NMR spectrum of **Si41** in C_6D_6 shows a strongly deshielded singlet signal at δ 402.4 ppm with ^{29}Si satellites ($^{1}J_{(\text{P,Si})}$ =170.4 Hz, 4.9%). The Si-$\text{C}_{\text{carbene}}$ bond distance is 1.960(2) Å.

Table 3

Key features of structurally characterized molecules consist of C_{NHC} Si bond (after reaction)

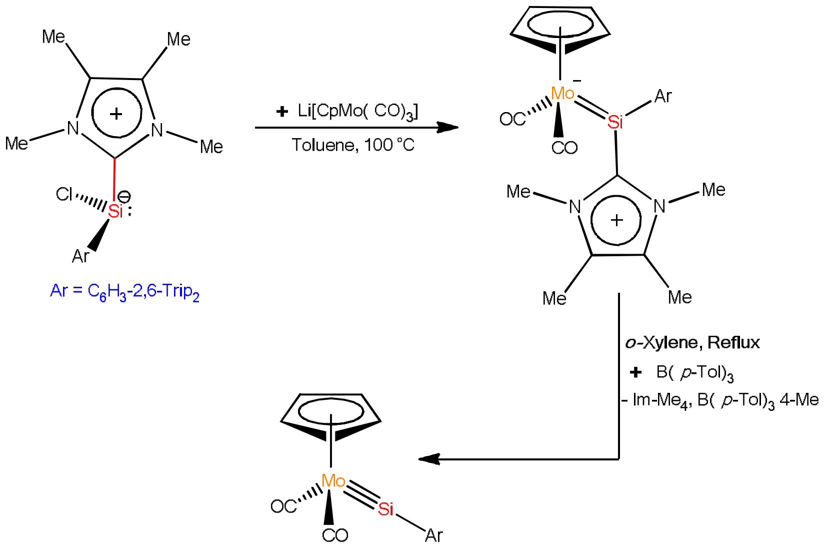
Molecule	Compound No.	^{13}C NMR of NCN, δ ppm	^{29}Si NMR of C-Si, δ ppm	C-Si separation, Å	Reference
	(Si37)	unknown	-53.19	1.965(5)	[11]

	(Si38)	unknown	30.72	1.937(2)	[19]
	(Si39)	unknown	-55.6	1.9284(15)	[29]
	(Si40)	208.05- 211.44	-6.56 to -7.89	~1.84	[38]
	(Si41)	unknown	267.3	1.960(2)	[39]

3.4 Reaction of NHC:SiX$_2$ (X = Cl,Br,I,R) with Transition Metal Substrates

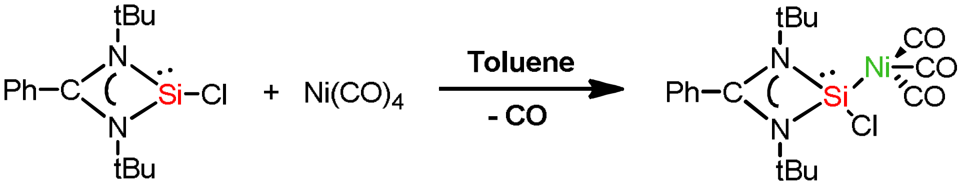
Filippou *et al.* in 2010 synthesised first metal silicon triple bond(silylidyne) using NHC stabilized aryl silicon(II) halide. Heating a toluene solution of SiArCl(ImMe$_4$), where Ar = C_6H_3-2,6-Trip$_2$ (Trip = C_6H_2-2,4,6-iPr$_3$) (**Si6**) and Li[CpMo(CO)$_3$] at 100 °C (Scheme 32) [14] gives the silylidene complex intermediate . IR Spectroscopic monitoring of reaction shows a rapid formation of intermediate complex. It is isolated after recrystallization in toluene-hexane solution as dark brown air sensitive solid with 51% yield.

The Mo-Si double bond length is 2.345 Å. The silicon centre is trigonal planar coordinated with Mo-Si-C$_{Ar}$ angle to be 145.3° showing steric effect of *m*-terphenyl group; and C$_{Ar}$-Si-C$_{carbene}$ angle to be 100.4° explaining low tendency of silicon for hybridisation. The Si-C$_{carbene}$ bond length is 1.944 Å which shows strong donor acceptor interaction. ^{1}H and ^{13}C{^{1}H} NMR spectrum reveals that the intermediate has C_S symmetric structure of the silylidene complex in solution. ^{13}C{^{1}H} NMR peak of the Ccarbene is at δ 165.3 ppm which is similar to **Si6** (δ 166.7 ppm) but upfield than that of Im-Me4 (δ 212.7 ppm). ^{29}Si{^{1}H} NMR signal appears downfield at δ 201.8 ppm. All this data signifies the zwitterionic structure of the intermediate as shown in Scheme 19.



Scheme 32. Reaction of Si6 to synthesize silylidyne complex (**Si42**) [14]

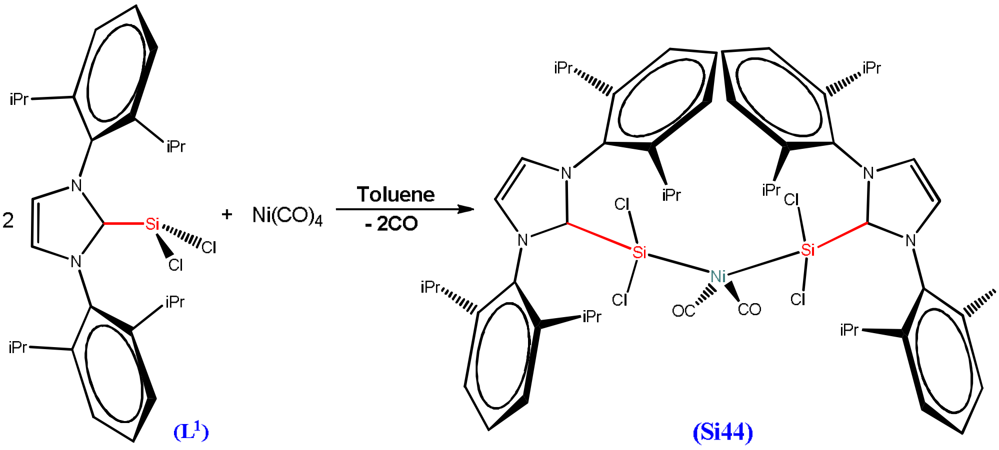
Further, refluxing this intermediate with triarylborane {B(C_6H_4-4-Me)$_3$} in *o*-xylene gives the silylidyne complex (**Si42**) and a carbene-borane adduct Im-Me$_4$. B(C_6H_4-4-Me)$_3$ (**4-Me**). **Si42** is separated from 4-Me by fractional crystallisation from pentane and is isolated as brick red; air sensitive solid; in 53% yield. This is an exoenergic process. **Si42** has almost C_S symmetry and is isostructural with its Germanium analogue. Mo-Si-C$_{Ar}$ angle is 173.49(8)° showing an almost linearly coordinated silicon centre. The Mo-Si triple bond length is 2.2241(7) Å. The $^{29}Si\{^1H\}$ NMR signal appears considerably downfield at δ 320.1 ppm than the intermediate. The IR spectrum in toluene shows 2 ν(CO) peaks at 1859 & 1785 cm^{-1} for silylidene complex and 1937 & 1875 cm^{-1} for silylidyne compex which is similar to its germanium analogue (1930 & 1875 cm^{-1}). This shows that silylidene ligand is weaker π-acceptor ligand than the silylidyne ligand in **Si42**. Also, the silylidyne and germylidyne ligand has similar σ-donor/π-acceptor ratio.



(L^3) **(Si43)**

Scheme 33. Synthesis of $L^3Ni(CO)_3$ (**Si43**)[15]

In 2010, Tavcar *et al.*, synthesised transition metal supported silylene derivatives. The ligand L^3 $^($PhC(NtBu)$_2$SiCl) have tri-coordinated silicon centre with one lone pair of electron. L^6 on reaction with Ni(CO)$_4$ (d^{10}, saturated ; labile and most reactive towards ligand exchange) in 1:1 molar ratio in toluene; yields $L^3Ni(CO)_3$ (**Si43**) (Scheme 33)[15]. The ^{29}Si NMR peak is at δ 62.69 ppm (downfield w.r.t. L^3, δ 14.16 ppm). The ^1H NMR shows two resonance peaks; one is of *t*Bu at δ 1.06 ppm (L^3; δ 1.08 ppm) and other is of phenyl protons at δ 6.71-6.95 ppm (L^3; δ 6.78-7.05 ppm). The ^{13}C NMR confirms the presence of carbonyl group resonating at δ 199.31 ppm. The CO-stretching frequencies are at 1984 cm^{-1} and 1969 cm^{-1}. **Si43** are colourless crystals with melting point 168-175 °C.

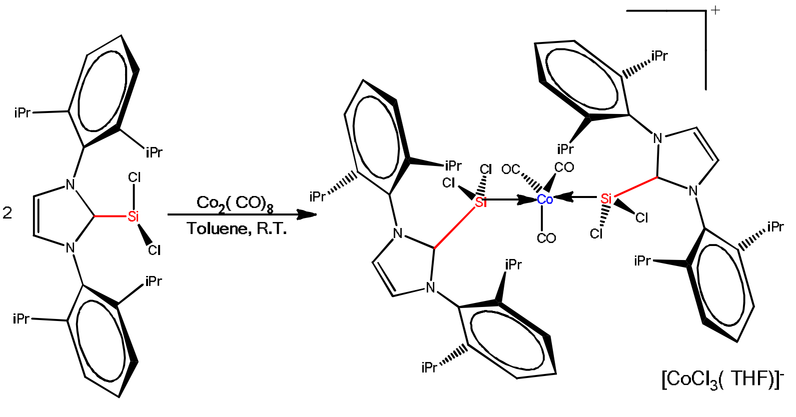


(L^1) **(Si44)**

Scheme 34. Synthesis of $L^1_2Ni(CO)_2$ (**Si44**)[15]

The ligand L^1 have tetra-coordinated silicon centre with one lone pair of electron. L^1 on reaction with $Ni(CO)_4$ in 2:1 molar ratio in toluene; yields $L^1_2Ni(CO)_2$ (**Si44**) (Scheme 34)[15]. The ^{29}Si NMR peak is at δ 43.19 ppm (downfield w.r.t. L^1, δ 19.06 ppm). The ^1H NMR shows three resonance peaks; first is of $-CH(CH_3)_2$ at δ 0.96 and 1.51 ppm (L^1; δ 1.01 and 1.43 ppm), second is of $-CH(CH_3)$2 at δ 2.94 ppm (L^1; δ 2.79 ppm) and third is of NC*H* at δ 6.23 ppm (L^1; δ 6.36 ppm). The ^{13}C NMR confirms the presence of carbonyl group resonating at δ 202.51 ppm. The CO-stretching frequencies are at 1974 cm^{-1} and 1921 cm^{-1}. **Si44** are bright yellow crystals with melting point 165-170 °C. On the basis of these wave numbers, the C-O bond energy in **Si43** is slightly higher as compared to **Si44**. This is in agreement with the fact that greater positive charge on nickel causes lesser back bonding of electron density into the π^* orbitals of CO ligand. Both the compounds, **Si43** and **Si44** crystallises in $P2_1/c$ space group. Silicon atom is terta-coordinated and silicon and nickel centres adopt distorted tetrahedral geometry in both. The Si-Ni bond lengths are 2.2111(8) Å in **Si43** and, 2.1955(9) Å and 2.1854(7) Å in **Si44**. This is 0.14 Å (Si11) and 0.16 Å (Si12) shorter than the sum of covalent radii of Si (1.11 Å) and Ni (1.24 Å).

Roesky *et al.*, in the same year, synthesised the first structurally described cobalt(I) Lewis-base-stabilized silylene complex $[Co(CO)_3\{SiCl_2(L^1)\}_2]^+[CoCl_3(THF)]^-$ (**Si45**) by applying the two-electron σ-donor ligand $SiCl_2(L^1)$ through coordination with $Co_2(CO)_8$ (Scheme 35)[16].

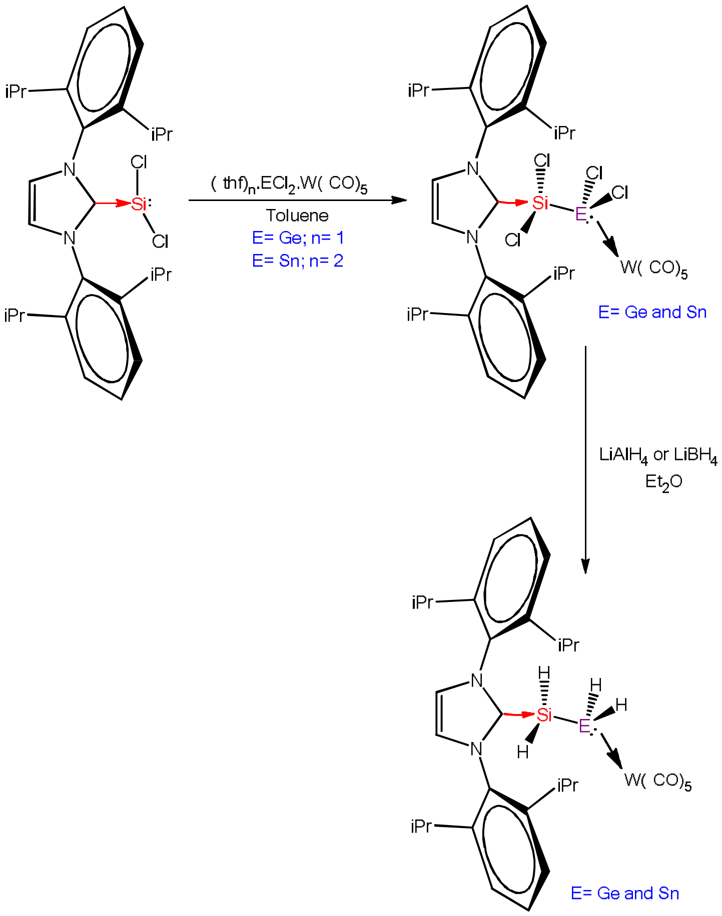


Scheme 35: Synthesis of $[Co(CO)_3\{SiCl_2(L^1)\}_2]^+ [CoCl_3(THF)]^-$ (**Si45**)[16]

Two eqivalents of L^1 reacts with $Co_2(CO)_8$ in toluene at room temperature to yield 74% of **Si45** (Scheme 35) [16] showing that **Si2** functions as a coordinate ligand as well as a chlorinating and a oxidising agent. The cationic part $[Co(CO)_3\{SiCl_2(L^1)\}_2]^+$ have C_2 symmetry and has distorted trigonal bipyramidal geometry with CO in the equatorial plane. Si-Co-Si is closely linear having cobalt in +1 formal oxidation state. The anionic part $[CoCl_3(THF)]^-$ is pseudotetrahedrally coordinated with Co in +2 formal oxidation state. The Co-Si bond lengths are 2.2278(13) Å and

2.2276(12) Å which is shorter than the covalently bonded Co-Si. The two silicon centres possess distorted tetrahedral geometry. **Si45** shows abnormal resonance in the ^{1}H NMR spectrum at room temperature due to the presence of d^{7} cobalt(II) tetrahedral anion and these resonance are shifted by different extent from δ +50 ppm at -90 °C and become broader at lower temperature. The $^{29}Si\{^{1}H\}$ NMR spectrum of **Si45** exhibited a singlet at δ 44.11 ppm which is 25.05 ppm downfield shifted than **Si2** (δ 19.06 ppm) which demonstrates the ambiphilicity of the Lewis-base-stabilized silylene in **Si45**.

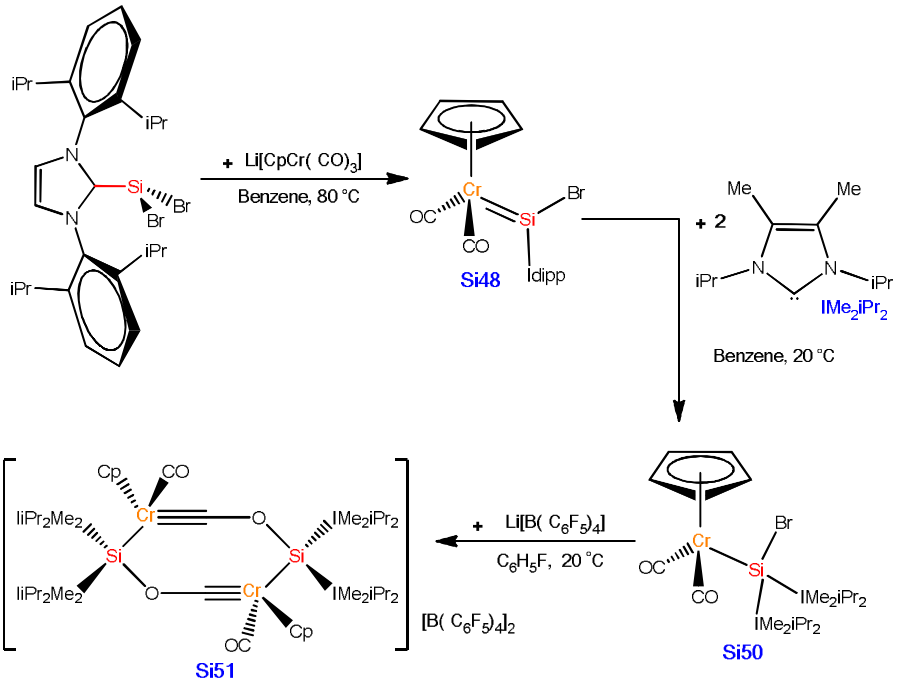
Ethylene is a very important precursor in many reactions but its heavier analogues ($R_2E{=}ER_2$; E= Ge, Sn or Pb) are hard to synthesize and stabilize but they are potential precursor in building new inorganic hybrid molecule. They are stabilized either by introducing a bulky group as R. Their bonding conditions are also totally different than regular olefins; as they can dissociate into two monomeric singlet R_2E: in solution and stays as *trans* bent geometry in solid state. In this direction, of making inorganic ethylene Rivard *et al.* in 2011 synthesized the first stable complex (at ambient temperature) H_2SiEH_2 (E= Ge and Sn). These $H_2E{=}EH_2$ (E= Si-Pb) complexes exists in *trans*-bent geometries and either of the centre can act as electron donor or acceptor which concludes that their isolation can be done in the presence of suitable Lewis acidic and basic groups.



Scheme 36: Synthesis of H_2SiEH_2(**Si46** & **Si47**)[22]

To make the Si-Ge and Si-Sn linkages, Roesky's Nucleophilic Si(II) halide **Si2** was reacted with the coordinatively labile tungsten complexes $[(thf)_n.ECl_2.W(CO)_5]$ (E= Ge & Sn). It gives the perhalogenated complex $[L^1Cl_2Si\text{-}ECl_2.W(CO)_5]$ (E= Ge & Sn). This on reduction using $LiAlH_4$ or $LiBH_4$ in diethyle ether gives the required inorganic ethylene adduct $[L^1H_2Si\text{-}EH_2.W(CO)_5]$ **Si46** (E=Ge) and **Si47** (E=Sn) (Scheme 36) [22]. They are air and moisture sensitive solids. **Si46** is thermally more stable than **Si47**, which decomposes even at low temperatures (-30° C).

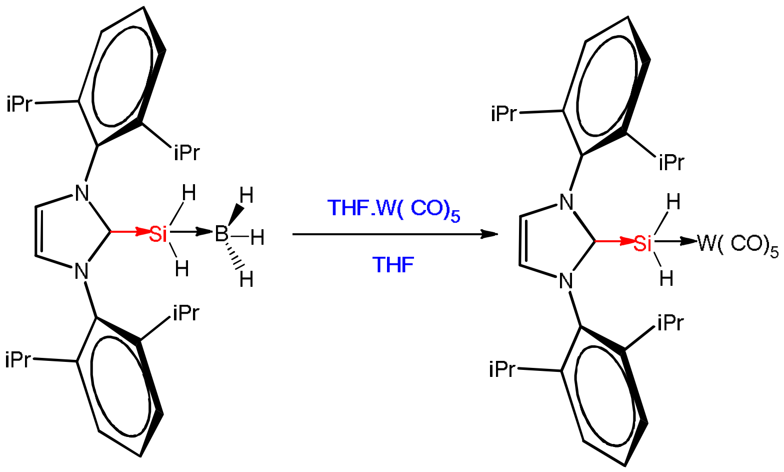
The Si-Ge bond distance in **Si46** is 2.3217(14) Å. The $C_{carbene}$-Si bond length is 1.915(5) Å which is shorter than **Si2**. ^1H NMR resonance appears as second order resonance at δ 3.73 and 1.90 ppm for SiH_2 and GeH_2, respectively in $[D_8]THF$, showing that the rotation of SiH_2 and GeH_2 groups is restricted in NMR timescale, making all the hydrides inequivalent. $^{29}Si\{^1H\}$ NMR resonance was detected at δ -71.9 ppm. The IR stretching bands of Si-H were at 2140 & 2150 cm^{-1} and of Ge-H were at 1959 cm^{-1}. **Si47** is nearly isostructural to **Si46** with Si-Sn bond distance to be 2.5808 Å. The $C_{carbene}$-Si bond length is 1.9128(17) Å which is similar to **Si46** showing a nearly same formally dative interaction. In both **Si-5** and **Si-6** the tungsten centre occupies quasi octahedral geometries. The IR stretching mode for Si-H was found at 2136 cm^{-1}. The Sn-H vibrations were not identified may be due to their low oscillator strengths. A very distinct NMR data was obtained for **Si47**. The $^{119}Sn\{^1H\}$ NMR spectrum shows a triplet of triplet at δ -537 ppm because of coupling between ^{119}Sn nuclei and hydrogen atom of SnH_2 and SiH_2.



Scheme 37: Synthesis of halosilylidyne and dinuclear siloxycarbyne complex (**Si48**, **Si49**, **Si50** & **Si-51**) using **Si3** and **Si2** [24]

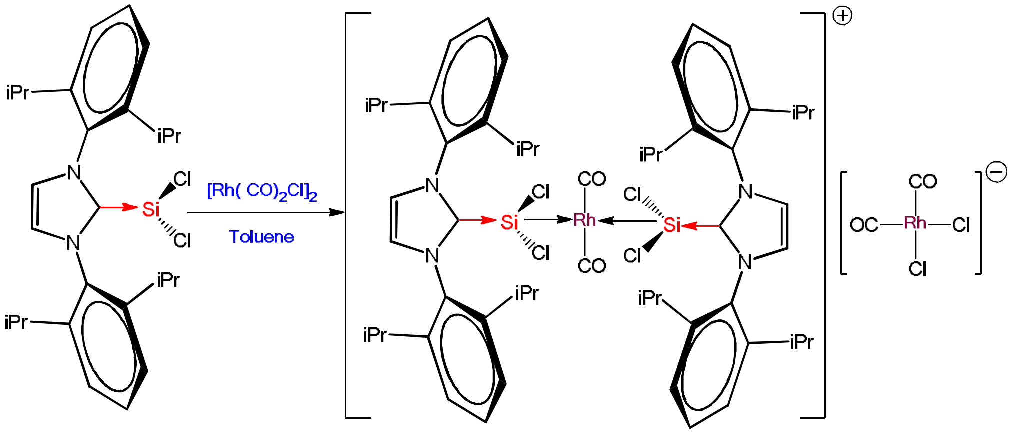
Si3 is a very good source of divalent silicon compound which is labile enough for nucleophilic reactions. This property was used by Filippou *et al.* in 2011 to make silylidene complex salt $[Cp(CO)Cr{=}Si(IMe_2iPr_2)_2][B(C_6F_5)_4]$, which further irreversibly dimerises to make the dinuclear siloxycarbyne complex $[Cp(CO)Cr\{(\mu\text{-}CO)Si((IMe_2iPr_2)_2\}_2Cr(CO)Cp][B(C_6F_5)_4]_2$ (**Si51**) by electrophilic activation of one carbonyl oxygen atom. **Si3** on reaction with $Li[CpCr(CO)_3]$ in benzene at 80° C makes NHC-stabilized bromosilylidyne ligand (**Si48**) (Scheme 37)[24]. Similarly **Si2** on reaction with $Li[CpCr(CO)_3]$ in benzene at 70° C gives the chloro congener of **Si48** *i.e.* **Si49**. **Si48** and **Si49** are dark brown and brown air sensitive crystalline solids respectively. The silicon centre in both is trigonal planar coordinated and uses the hybrid orbital with high p character for σ-bonding with Br/Cl. The Cr-Si bond distances are 2.01618(9) Å and 2.1603(7) Å in **Si48** and **Si49**, respectively. The Si-Br and Si-Ccarbene bond distances are 2.2728(8) Å and 1.957(3) Å. The IR spectra in fluorobenzene shows two ν(CO) peaks at 1894 & 1809 cm^{-1} for **Si48** and 1890 & 1806 cm^{-1} for **Si49** showing the presence of an electron rich metal centre pursuing strong metal carbonyl back-bonding.

The reaction of **Si48** with two equivalents of 1,3-dihydro-4,5-dimethyl-1,3-bis(isopropyl)-2*H*-imidazole-2ylidene (IMe_2iPr_2) in benzene at 20° C gives another class of silylidyne **Si50**. It is isolated in 88% yield as a red-brown crystalline air-sensitive solid which decomposes over 166-168° C. The reaction proceeds via addition-elimination reaction sequence. There is a considerable shift in the ν(CO) absorption band to lower wavenumbers (1797 & 1733 cm^{-1}) in THF because of the presence of two NHC, hereby, indicating stronger Cr-CO back-bonding than **Si48**. ^{29}Si NMR spectrum in $[D_8]$THF appears as a singlet signal at δ 17.3 ppm which is at higher field than **Si48** at δ 95.1 ppm. It has C_1 symmetric minimum structure because of the frozen rotation of NHC at low temperature. The Cr-Si bond distance is 2.2515(7) Å. The Si-Ccarbene bond's average bond distance is 1.979 Å. Also the Si-Br bond length is 2.4340(6) Å which is significantly longer, depicting the more polar Si-Br bond. When one equivalent of $Li[B(C_6F_5)_4]$ is added to **Si50** in fluorobenzene at ambient temperature, LiBr is rapidly precipitated. IR monitoring of this reaction reveals the formation of $[Cp(CO)_2Cr{=}Si(IMe_2iPr_2)_2][B(C_6F_5)_4]$ with ν(CO) at 1895 & 1821 cm^{-1} which is considerably higher wavenumber than **Si50** and is similar to **Si49**. This complex is non-isolable and dimerises rapidly at -16° C to a insoluble yellow dinuclear siloxycarbyne complex salt **Si51**. It shows only one IR peak for CO ligand, displaying them to be equivalent, at 1860 cm^{-1} which lies in terminal CO region.



Scheme 38. Synthesis of L^{1}SiH$_2$.W(CO)$_5$ complex (**Si52**)[29]

Rivard *et al.* in 2012, synthesised the L^1.SiH$_2$.BH$_3$ adduct (**Si39**). This Si(II) dihydride has a great tendency of electron donation. To show this, they combined **Si39** with THF.W(CO)$_5$. This readily gave a stable tungsten complex L^1.SiH$_2$.W(CO)$_5$ (**Si52**) with loss of THF.BH$_3$ (Scheme 38)[29]. The yield was reported as 66%. In the IR spectrum two sharp bands at 2086 cm^{-1} for ν_{sym} and 2107 cm^{-1} for ν_{asym} stretching mode. The *trans* CO ligand at tungsten gives characterstic A_1 vibration at 2044 cm^{-1}. DFT studies shows that the Si-W bond is polarised with more electron density at silicon. The Si-Ccarbene bond distance is 1.928(13) Å and the Si-W bond distance is 2.573(4) Å.

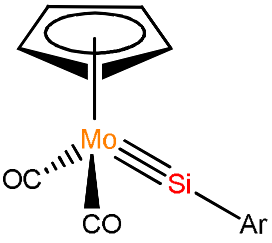
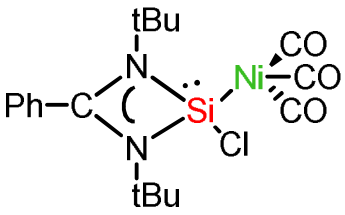
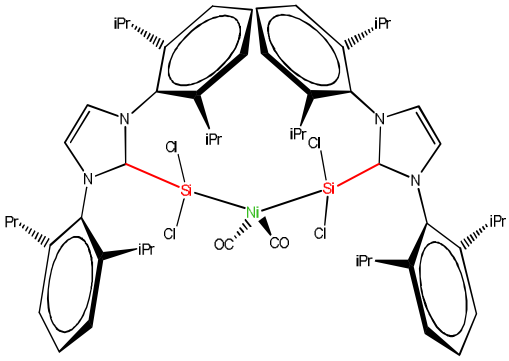
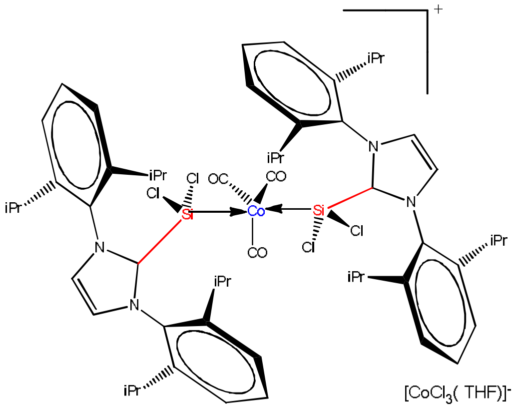


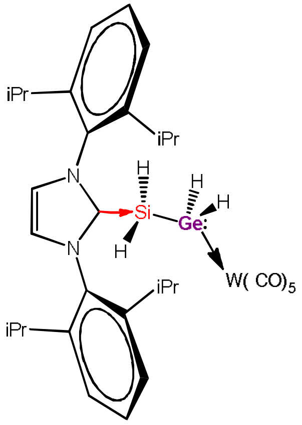
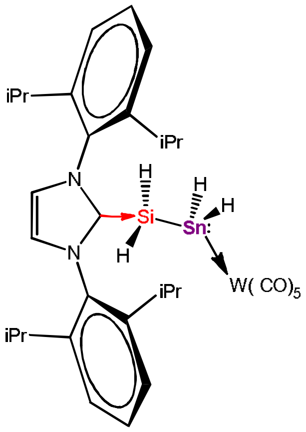
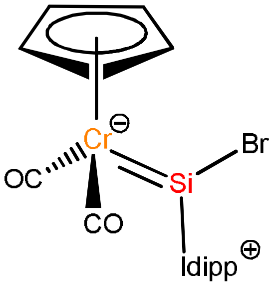
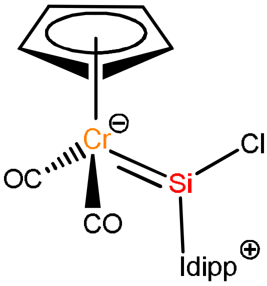
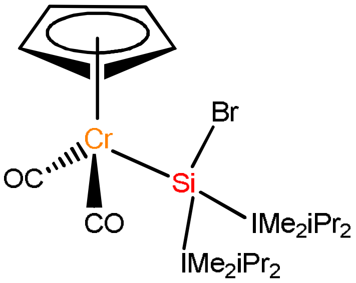
Scheme 39. Synthesis of *trans*-[(L^1.SiCl$_2$)$_2$Rh(CO)$_2$]$^+$ *cis*-[Rh(CO)$_2$Cl$_2$]$^-$ (**Si53**)[29]

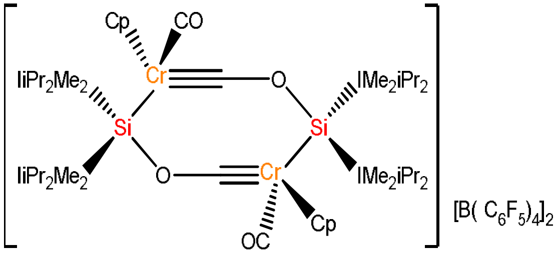
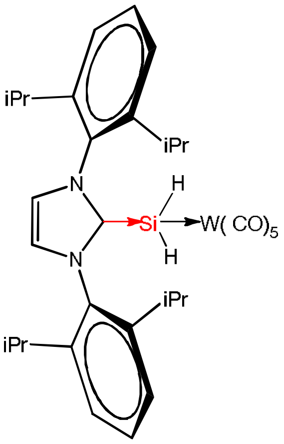
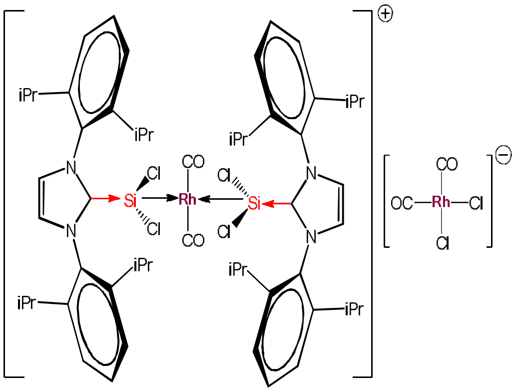
The same group then produced a stable Rh-Silylene complex, *trans*-[(L^1.SiCl$_2$)$_2$Rh(CO)$_2$]$^+$ *cis*-[Rh(CO)$_2$Cl$_2$]$^-$ (**Si53**) as an orange crystalline solid, by reacting **Si2** with excess [Rh(CO)$_2$Cl]$_2$ in toluene, isolated in 87% yield (Scheme 39)[29]. It is a coordination isomer of [L^1.SiCl$_2$.Rh(CO)$_2$Cl]. The ^{13}C{^{1}H} NMR shows two distinct CO peaks displaying two different environment. The average Si-C$_{carbene}$ and Si-Rh bond distances are 1.939(3) Å and 2.3605(8) Å, respectively.

Table 4

Key features of structurally characterized molecules consist of C_{NHC} Si bond (after reaction)

Molecule	Compound No.	^{13}C NMR of NCN, δ ppm	^{29}Si NMR of C-Si, δ ppm	C-Si separation, Å	Reference
 Ar = C_6H_3-2,6-Trip$_2$	(Si42)	unknown	320.1	Not present	[14]
	(Si43)	Not present	62.69	Not present	[15]
	(Si44)	unknown	43.19	1.985(2) and 2.002(2)	[15]
	(Si45)	unknown	44.11	unknown	[16]

	(Si46)	unknown	-71.9	1.915(5)	[22]
	(Si47)	unknown	unknown	1.9128(17)	[22]
	(Si48)	unknown	95.1	1.957(3)	[24]
	(Si49)	unknown	unknown	unknown	[24]
	(Si50)	unknown	17.3	1.979	[24]

	(Si51)	Not present	Not present	Not present	[24]
	(Si52)	unknown	unknown	1.928(13)	[29]
	(Si53)	unknown	unknown	1.939(3)	[29]

Chapter 4

Summary and conclusion

The isolation of N-heterocyclic carbenes (NHCs) by Arduengo introduced an unusually versatile class of compounds which proved to be an excellent ligand for stabilizing mono- and diatomic species. Also, the halosilylenes (:SiX_2) serves a widespread role in the field of inorganic as well as organic synthesis. The addition of NHC gives a great electronic support to the reactive and unstable SiX_2, which leads to the stabilization and isolation of NHC→ SiX_2 as solid at room temperature. These solids are mostly crystalline and are stable at room temperature. The stability and crystallinity depends on the NHC and the parent halosilylene. This facilitated an easier access to the Si(II) systems for many reactions, which includes insertion of silicon. To account this many NHC's were used to stabilize :SiX_2. These systems acts as structural motifs to monomeric :SiX_2 and gives similar reactions as :SiX_2 under suitable reaction conditions. The bond formed (Si-$C_{carbene}$) is polar and hence is strong, yet it is labile enough to be removed. Thus, it acts as free :SiX_2. Better is the donation from NHC, better bonds are formed between Si-$C_{carbene}$. The silicon center in NHC→ SiX_2 has lone pair as well as vacant orbitals which make it very facile and reactive. The NHC-SiX_2 acts as both Lewis acid (electrophile) and Lewis base (nucleophile). This ambiphilicity leads to its extensive reactivity and ability to form unstable compouds with considerable stability and activity. Si-E (metal, main group) bonds are also synthesized using it. It facilitates synthesis of many silicon analougues of carbon compounds such as silylidenes, silylidynes (π bonds), silallenes, etc are made with ease at normal conditions.

Thus, we conclude that, the synthesis of N-Heterocyclic Carbene supported Halosilylene proved to be a landmark in the field of silicon chemistry. It provided an easy way of isolating many rare and unknown silicon analogues of carbon compounds. Si-Si multiple bonds, silicon bonded with main group elements and transition metals are also synthesised using this precursor. This area of research is growing and advancing progressively. This will lead to the synthesis and practicing of many more unknown useful low valent silicon compounds and precursors.

References

[1] R. West, M. Denk, *Pure* & *Appl. Chem.* 68(1996) 785.

[2] M.N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature*, 510 (2014) 485.

[3] C.M. Crudden, D.P. Allen, *Coordination Chemistry Reviews 248 (2004) 2247.*

[4] M. Haaf, T.A. Schmedake, R. West, *Acc. Chem. Res.* 33(2000**)** 704.

[5] N.J. Hill, R. West, *J. of Organo. Chem.* 689 (2004) 4165.

[6] B. Blom, D. Gallego, M. Driess, *Inorg. Chem. Front.*, 1 (2014) 134.

[7] M. E. Lee, H.M. Cho, M.S. Ryu, C.H. Kim, W. Ando, *J. Am. Chem. Soc.*, 123 (2001) 7732.

[8] Y. Wang, Y. Xie, P. Wei, R.B. King, H. F. Schaefer III , P.V.R. Schleyer, G.H. Robinson, *Science* 321 (2008).

[9] R.S. Ghadwal, H.W. Roesky, S. Merkel, J. Henn, D. Stalke, *Angew. Chem. Int. Ed.* 48 (2009) 5683.

[10] A.C. Filippou, O. Chernov, G. Schnakenburg, *Angew. Chem. Int. Ed.* 48 (2009) 5687.

[11] R.S. Ghadwal, H.W. Roesky, S. Merkel, D. Stalke, *Chem. Eur. J.* 16 (2010) 85.

[12] A.C. Filippou, O. Chernov, B. Blom, K.W. Stumpf, G. Schnakenburg, *Chem. Eur. J.* 16 (2010) 2866.

[13] R.S. Ghadwal, S.S. Sen, H.W. Roesky, M. Granitzka, D. Kratzert, S. Merkel, D. Stalke, *Angew. Chem. Int. Ed.* 49 (2010) 3952.

[14] A.C. Filippou, O. Chernov, K.W. Stumpf, G. Schnakenburg, *Angew. Chem. Int. Ed.* 49 (2010) 3296.

[15] G. Tavcar, S.S. Sen, R. Azhakar, A. Thorn, H.W. Roesky, *Inorg. Chem.* 49 (2010) 10199.

[16] J. Li, S. Merkel, J. Henn, K. Meindl, A. Doring, H.W. Roesky, R.S. Ghadwal, D. Stalke, *Inorg. Chem.* 49 (2010) 775.

[17] R.S. Ghadwal, S.S. Sen, H.W. Roesky, M. Granitzka, S. Merkel, D. Stalke, *J. Am. Chem. Soc.* 132 (2010) 10018.

[18] R.S. Ghadwal, S.S. Sen, H.W. Roesky, C. Schulzke, M. Granitzka, *Organometallics* 29 (2010) 6329.

[19] R. Azhakar, G. Tavcar, H.W. Roesky, J. Hey, D. Stalke, *Eur. J. Inorg. Chem.,* (2011) 475.

[20] R.S. Ghadwal, S.S. Sen, H.W. Roesky, K. Propper, B. Dittrich, S. Klein, and G. Frenking, *Angew. Chem. Int. Ed.* 50 (2011) 5374.

[21] H. Tanaka, S. Inoue, M. Ichinohe, M. Driess, A. Sekiguchi, *Organometallics* 30 (2011) 3475.

[22] S.M. Ibrahim Al-Rafia, A.C. Malcolm, R. McDonald, M.J. Ferguson, E. Rivard, *Angew. Chem. Int. Ed.* 50 (2011) 8354.

[23] Haiyan Cui, Chunming Cui, *Dalton Trans.* 40 (2011) 11937.

[24] A.C. Filippou, O. Chernov, G. Schnakenburg, *Chem. Eur. J.* 17 (2011) 13574.

[25] A.C. Filippou, B. Baars, O. Chernov, Y.N. Lebedev, G. Schnakenburg, *Angew. Chem. Int. Ed.*, 53 (2014) 565.

[26] S.M. Ibrahim Al-Rafia, R. McDonald, M.J. Ferguson, E. Rivard, *Chem. Eur. J.* 18 (2012) 13810.

[27] R.S. Ghadwal, R. Azhakar, H.W. Roesky, K. Propper, B. Dittrich, C. Goedecke, G Frenking, *Chem. Commun.,* 48 (2012) 8186.

[28] Y. Xiong, S. Yao, S. Inoue, E. Irran, M. Driess, *Angew. Chem. Int. Ed.* 51 (2012) 10074.

[29] S.M.I. Al-Rafia, A.C. Malcolm, R. McDonald, M.J. Ferguson, E. Rivard, *Chem. Commun.,* 48 (2012) 1308.

[30] H. Cui, B. Ma, C. Cui, *Organometallics* 31 (2012) 7339.

[31] P.P. Samuel, R. Azhakar, R.S. Ghadwal, S.S. Sen, H.W. Roesky, M. Granitzka, J.Matussek, R.Herbst-Irmer, D. Stalke, *Inorg. Chem.* 51 (2012) 11049.

[32] K.C. Mondal, H.W. Roesky, M.C. Schwarzer, G. Frenking, I. Tkach, H. Wolf, D. Kratzert, R. H. Irmer, B. Niepçtter, D. Stalke, *Angew. Chem. Int. Ed.* 52 (2013) 1801.

[33] A.P Singh, P.P. Samuel, K.C. Mondal, H.W. Roesky, N.S. Sidhu, B. Dittrich, *Organometallics* 32 (2013) 354.

[34] K.C. Mondal, P.P. Samuel, M. Tretiakov, A.P. Singh, H.W. Roesky, A.C. Stuckl, B. Niepotter, E. Carl, H. Wolf, R. Herbst-Irmer, D. Stalke, *Inorg. Chem.* 52 (2013) 4736.

[35] A.C. Filippou, Y.N. Lebedev, O. Chernov, M. Straßmann, G. Schnakenburg, *Angew. Chem. Int. Ed.* 52(2013) 6974.

[36] Y. Xiong, S. Yao, S. Inoue, J.D. Epping, M. Driess, *Angew. Chem. Int. Ed.* 52 (2013) 7147.

[37] Y.N. Lebedev, U. Das, O. Chernov, G. Schnakenburg, A.C. Filippou, *Chem. Eur. J.* 20 (2014) 9280.

[38] S. Roy, P. Stollberg, R.H. Irmer, D. Stalke, D.M. Andrada, G. Frenking, H.W. Roesky, *J. Am. Chem. Soc.* 137 (2015) 150.

[39] D. Geiß, M.I. Arz, M. Straßmann, G. Schnakenburg, A.C. Filippou, *Angew. Chem. Int. Ed.* 54 (2015) 2739.

[40] N. Holzmann, D.M. Andrada, G. Frenking, *J. of Organo. Chem.*, 792 (2015) 139.