ACCOUNTS
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Dichlorosilylene: A High Temperature Transient Species to an Indispensable Building Block

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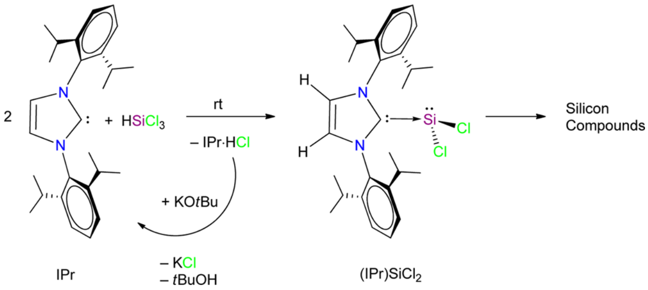
CONSPECTUS



Isolating stable compounds with low-valent main group elements have long been an attractive research topic, because several of these compounds can mimic transition metals in activating small molecules. In addition, compounds with heavier low-valent main group elements have fundamentally different electronic properties when compared with their lighter congeners. Among group 14 elements, the heavier analogues of carbenes (R_2C:) such as silylenes (R_2Si:), germylenes (R_2Ge:), stannylenes (R_2Sn:), and plumbylenes (R_2Pb:) are the most studied species with low-valent elements. The first stable carbene and silylene species were isolated as N-heterocycles. Among the dichlorides of group 14 elements, CCl_2 and $SiCl_2$ are highly reactive intermediates and play an important role in many chemical transformations. $GeCl_2$ can be stabilized as a dioxane adduct, whereas $SnCl_2$ and $PbCl_2$ are available as stable compounds.

In the Siemens process, which produces electronic grade silicon by thermal decomposition of $HSiCl_3$ at 1150 °C, chemists proposed dichlorosilylene ($SiCl_2$) as an intermediate, which further dissociates to Si and $SiCl_4$. Similarly, base induced disproportionation of $HSiCl_3$ or Si_2Cl_6 to $SiCl_2$ is a known reaction. Trapping these products in situ with organic substrates suggested the mechanism for this reaction. In addition, West and co-workers reported a polymeric *trans*-chain like perchloropolysilane $(SiCl_2)_n$. However, the isolation of a stable free monomeric dichlorosilylene remained a challenge. The first successful attempt of taming $SiCl_2$ was the isolation of monochlorosilylene $PhC(N\textit{t}Bu)_2SiCl$ supported by an amidinate ligand in 2006.

In 2009, we succeeded in isolating N-heterocyclic carbene (NHC) stabilized dichlorosilylene $(NHC)SiCl_2$ with a three coordinate silicon atom. (The NHC is 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) or 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes).) Notably, this method allows for the almost quantitative synthesis of $(NHC)SiCl_2$ without using any hazardous reducing agents. Dehydrochlorination of $HSiCl_3$ with NHC under mild reaction conditions produces $(NHC)SiCl_2$. We can separate the insoluble side product (NHC)HCl readily and recycle it to form NHC. The high yield and facile access to dichlorosilylene allow us to explore its chemistry to a greater extent.

In this Account, we describe the results using $(NHC)SiCl_2$ primarily from our laboratory, including findings by other researchers. We emphasize the novel silicon compounds, which supposedly existed only as short-lived species. We also discuss silaoxirane, silaimine with tricoordinate silicon atom, silaisonitrile, and silaformyl chloride. In analogy with N-heterocyclic silylenes (NHSis), oxidative addition reactions of organic substrates with $(NHC)SiCl_2$ produce Si(IV) compounds. The presence of the chloro-substituents both on $(NHC)SiCl_2$ and its products allows metathesis reactions to produce novel silicon compounds with new functionality. These substituents also offer the possibility to synthesize interesting compounds with low-valent silicon by further reduction. Coordination of NHC to the silicon increases the acidity of the backbone protons on the imidazole ring, and therefore $(NHC)SiCl_2$ can functionalize NHC at the C-4 or C-5 position.

1. Introduction and Background

Silylenes are compounds with divalent neutral silicon with a lone pair of electrons. They are key intermediates in various photochemical, thermal, and metal reduction reactions of organosilicon compounds.[1−3] The isolation of the first stable NHSi was reported by West and co-workers in 1994.[4]

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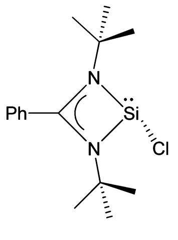
The silylene of West is a silicon analogue of Arduengo's NHC.[5] Since then, an appreciable number of silylenes have been reported,[6−8] and their chemistry has been studied. It is worth mentioning that all these silylenes are NHSis with variable ring size and are stabilized by adjacent amino-nitrogen atoms with the exception of Kira's kinetically stabilized cyclic dialkylsilylene.[9] Very recently two acyclic silylenes with two-coordinate silicon atom were reported.[10,11]

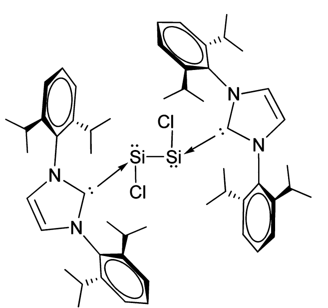
Among dihalosilylenes, gaseous dichlorosilylene has been known for many years; however, at room temperature, it condenses to polymeric $(SiCl_2)_n$ or disproportionates to Si and $SiCl_4$. Schmeisser[12] and Schenk[13] described the properties of the polymeric $(SiCl_2)_n$ already in 1964. In 1968, Timms[14] carried out some reactions of condensed $(SiCl_2)_n$ with acetylene and benzene which resulted in brown polymeric products of unknown composition. There have been few more reports on the synthesis and properties of cyclic and linear polydichlorosilanes.[15] A polymeric *trans*-chain like perchloropolysilane $(SiCl_2)_n$ was reported by West and co-workers[16] in 1998, which is insoluble in organic solvents and no solution study is available. The single crystal X-ray structure of this compound with a *R* value of 18 is discussed.

Early reports on (i) trichlorosilylmetal compounds in which they undergo α-elimination[17] of metal chloride like Seyferths CCl_2 source ($PhHgCCl_3$), (ii) thermodynamically unfavorable α-elimination[18] of HCl from $HSiCl_3$, and (iii) α-elimination[19] of $SiCl_4$ from Si_2Cl_6 have revealed "hidden $SiCl_2$ functions". Base induced disproportionation of Si_2Cl_6 resulted in the formation of highly branched polysilanes and $SiCl_4$. Various mechanisms have been proposed for this disproportionation; however, an exact mechanism is not known. As a synthetic alternative to compounds containing the $SiCl_2$ moiety, transient $SiCl_2$ generated in situ by the treatment of $HSiCl_3$ with tertiary amines and the trapping products with different unsaturated organic compounds were reported by Benkeser.[20] He postulated the existence of the trichlorosilyl anion ($SiCl_3^-$) as an intermediate in these transformations. Jung and co-workers reported[21] the trapping of $SiCl_2$, which was generated by the reaction of $HSiCl_3$ with phosphonium chloride in a stainless steel cylinder at 150 or 180 °C, in the presence of conjugated dienes or by an alkyne. In their proposed mechanism, the involvement of $SiCl_2$ or $SiCl_3^-$ as intermediates was discussed but none of these species were isolated. Of course, efforts of making a stable version of a very reactive species using a donor- or an acceptor-ligand may cause a change of its chemical behavior. Nevertheless, how an unstable species is stabilized is a matter of keen interest for the scientific and industrial community. The taming of a $SiCl_2$ derivative was first reported in 2006.[22] A monochlorosilylene[22] (PhC(N*t*Bu)$_2$SiCl) (**1**) was stabilized by an amidinate ligand resulting in a three-coordinate silicon atom. However, access to dichlorosilylenes that are stable at room temperature has remained a challenge until 2009 (Chart 1).

CHART 1. Stable Chlorosilylenes



1



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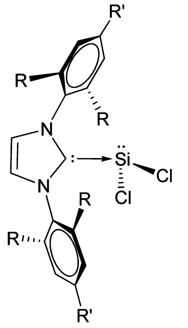
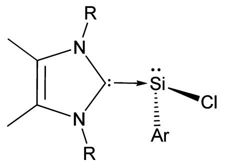


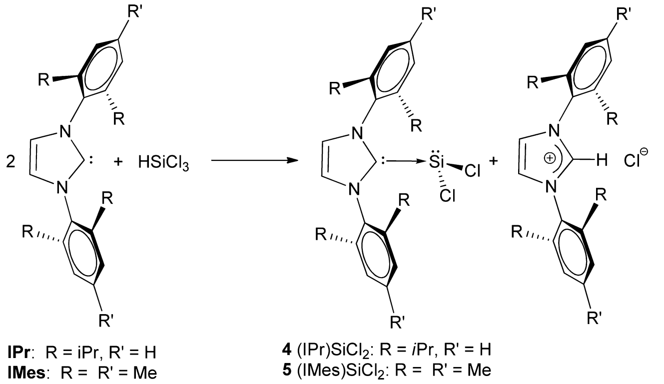
4 (IPr)SiCl$_2$: R = *i*Pr, R' = H
5 (IMes)SiCl$_2$: R = R' = Me



6a: R = Me, Ar = 2,6-(2,4,6-Me$_3$C$_6$H$_2$)$_2$C$_6$H$_3$
6b: R = Me, Ar = 2,6-(2,4,6-*i*Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$
6c: R = *i*Pr, Ar =(2,6-*i*Pr$_2$C$_6$H$_3$)N(SiMe$_3$)

Strong σ-donor and weak π-acceptor properties of NHCs have been exploited in the recent decades not only to stabilize compounds with main group elements in low-oxidation states[23] but also as HCl scavengers to prepare metal hydroxides.[24] NHC as a ligand in silicon chemistry was first introduced by Kuhn and co-workers.[25] Robinson and co-workers employed[26] a bulky NHC (IPr) and reported the (IPr)SiCl$_4$, which on reduction with KC$_8$ affords bis(monochlorosilylene) [(IPr)SiCl]$_2$ (**2**) along with a diatomic silicon(0) compound [(IPr)Si]$_2$ (**3**). Compounds **2** and **3** were isolated in 5−30% yield. Surprisingly, the formation of (IPr)SiCl$_2$ was not observed. A successful synthesis of a dichlorosilylene that is stable at normal laboratory conditions was achieved in 2009.[27] The dichlorosilylene adducts (NHC)SiCl$_2$ (NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) **4**; NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) **5**)[27] were isolated and structurally characterized. A dibromosilylene (IPr)SiBr$_2$ was prepared subsequently by Fillipou and co-workers.[28] Three NHC stabilized monochlorosilylenes (**6a**−**6c**) have been reported (Chart 1).[29]

SCHEME 1. Synthesis of Dichlorosilylenes **4** and **5** by Reductive Dehydrochlorination of Trichlorosilane



2. Synthesis, Spectroscopic, and Structural Properties of Dichlorosilylenes (NHC)$SiCl_2$

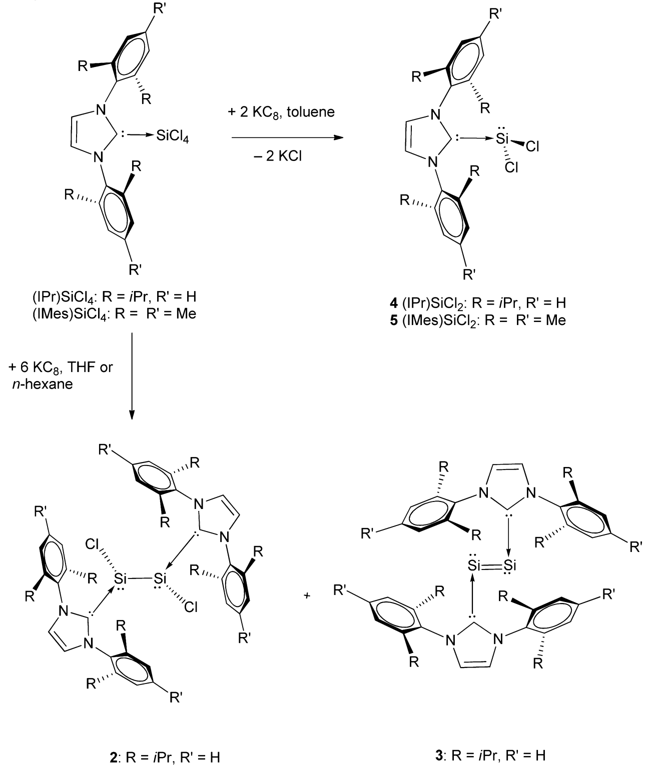
Treatment of $HSiCl_3$ with 2 equiv of NHC (IPr or IMes) yields (IPr)$SiCl_2$ (**4**) or (IMes)$SiCl_2$ (**5**).[27] Compounds **4** and **5** are formed under mild reaction conditions by reductive elimination of HCl from trichlorosilane in the presence of the NHC (Scheme 1) and were isolated in >70% yield.

Robinson and co-workers[26] isolated compounds [(IPr)SiCl]$_2$ (**2**) and [(IPr)Si]$_2$ (**3**) on reduction of (IPr)$SiCl_4$ with an excess of KC_8 (Scheme 2). Surprisingly, formation of (IPr)$SiCl_2$ (**4**) was not observed. Interestingly, reaction of (IPr)$SiCl_4$ and KC_8 in 1:2 molar ratio in toluene (Scheme 2) gave (IPr)$SiCl_2$ (**4**) in moderate yield (48%).[27]

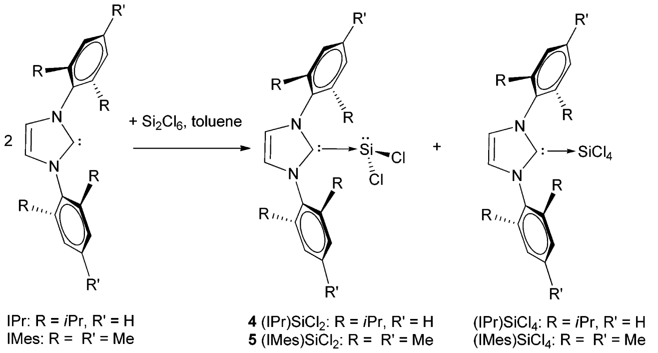
Base induced disproportionation of Si_2Cl_6 is well-known. Treatment of Si_2Cl_6 with NHC affords (NHC)$SiCl_2$ (NHC is IPr **4**, or IMes **5**) and (NHC)$SiCl_4$ which provides a clear evidence of disproportionation of Si_2Cl_6 to $SiCl_2$ and $SiCl_4$ (Scheme 3).[30] This alternative method was also employed successfully to isolate PhC(N*t*Bu)$_2$SiCl (**1**) and PhC(N*t*Bu)$_2$SiCl$_3$.[30]

Compounds **4** and **5** are stable under an inert atmosphere and no noticeable changes in their NMR spectra were observed after storage for two months. They react readily with moisture and air to form the corresponding (NHC)HCl salt. **4** and **5** exhibit ^{29}Si NMR resonances at δ 19.06 and 17.84 ppm which are consistent with that observed for monochlorosilylene **1** (δ 14.6).[22] The solid state characterization of **4** by single crystal X-ray study reveals a distorted trigonal pyramidal geometry at the three-coordinate silicon atom with the stereochemically active lone pair of electrons at the apex (Figure 1). The sum of the bond angles at the silicon atom in **4** (289.75°; compare with 291.09° in the gas phase optimized structure) is significantly smaller than that in **2** (308.08°) but larger than that in **1** (260.74°). The Si–C bond length (1.985(4) Å) in **4** is slightly longer than that reported for (IPr)$SiCl_4$ (1.928(2) Å) and **3** (1.934(6) Å).

SCHEME 2. Conventional Synthesis of Dichlorosilylene (**4**, **5**) and Disilylene (**2**, **3**)



SCHEME 3. Base-Induced Disproportionation of Si_2Cl_6 to $SiCl_2$ and $SiCl_4$ as Stable NHC Adducts



3. Facile Access to Novel Silicon Compounds with (IPr)$SiCl_2$ (4)

Availability of the first NHC stabilized dichlorosilylene **4** as a stable compound in high yield by a straightforward synthetic method offers a unique opportunity to explore not only its chemical nature but also provides a convenient route to access unusual silicon compounds. Apart from some typical

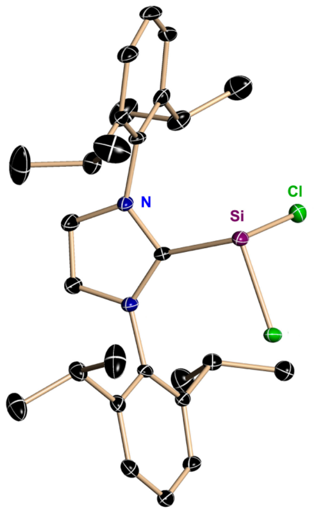


FIGURE 1. Molecular structure of **4**.

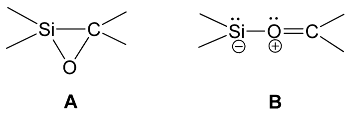
reactivity, like NHSis, one can expect some distinct results in the case of **4** and **5**. Among some interesting outcomes, isolation of monosiliconepoxides, silaisonitrile, silaformyl chloride, silicon(II) hydride (SiH_2), and alkene analogues (SiH_2EH_2, E = Sn or Ge) are discussed. Silylenes can in principle behave as Lewis acids as well as Lewis bases, and are of ambiphilic nature.[31] Lewis acidic behavior of a silylene ($SiCl_2$ in this case) has been demonstrated in **4** and **5**, where a Lewis base NHC forms an adduct and stabilizes the $SiCl_2$. Coordination of **4** with a Lewis acid (e.g., borane) provides a unique example featuring Lewis base and Lewis acid character of a silylene. Oxidative addition reactions of **4** with organic substrates and H_2O are reported as well as reactions of **4** as a neutral σ-donor ligand for transition metals are mentioned. Moreover, fuctionalization of NHC, interaction with muon, and metathesis reactions of **4** are presented.

i. Reaction with Ketone to Access Monosiliconepoxide. The involvement of either monosiliconepoxide (or silaoxirane) **A**, a three-membered ring compound with Si, O, and C atoms, or silacarbonyl ylide **B** (Chart 2) as intermediates[32] in the reaction of transient or stable silylenes with carbonyl compounds was proposed.

Computational studies revealed that neutral silaoxiranes should be strongly stabilized by adding an anion like fluoride.[33] Interestingly, [1 + 2]-cycloaddition reactions of **4** with ketones afford stable silaoxiranes **7** and **8** (Scheme 4).[34] Compounds **7** and **8** are the first examples of silaoxirane containing a five-coordinate silicon atom and are stabilized by the σ- donating NHC ligand. Reaction of **4** with benzil (PhCOCOPh) results in [1 + 4]-cycloaddition product **9** (Scheme 4).[34]

^{29}Si NMR resonance in the δ −99 to −123 ppm region supports the presence of a five-coordinate silicon atom in each of **7**–**9**. The molecular structure of **7** is shown in Figure 2. The Si$\leftarrow$C bond length in **7** (1.9653(15) Å) is comparable with that found in **4** (1.985(4) Å). The Si–Cl bond lengths in **7** are noticeably shorter than the average bond length in **4**. The three-membered strained rings each in **7** and **8** consist of nonisosceles triangles.

CHART 2. Silaoxirane (**A**) and Silacarbonyl Ylide (**B**)

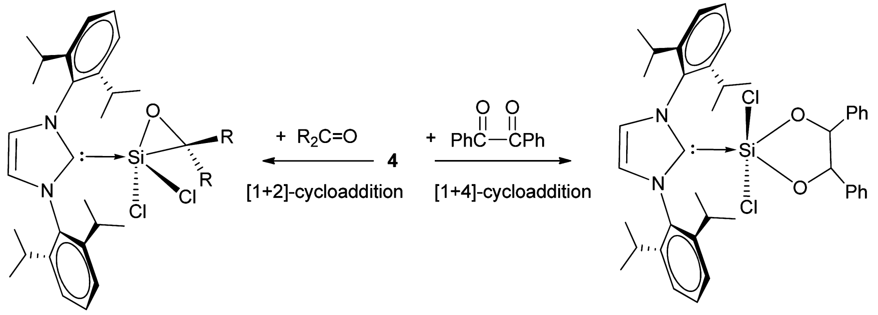


ii. Reaction with Organic Azides and Carbodiimides. Compounds with a multiple bond to silicon are of special interest.[35] Silaimines are compounds with a silicon–nitrogen double bond. Reaction of a silylene with an organic azide provides an alternative to silaimine. However, such reports are very rare and no halosilaimine was isolated so far. The polarity of the Si=N bond and the presence of electronegative chloro-substituents make the silicon atom very electron deficient and may be the reason of the instability. The electron donation by a NHC ligand to the silicon atom may compensate this deficiency and stabilize a chlorosilaimine. Compound **4** reacts with bulky organic azides to afford NHC stabilized dichlorosilaimines **10** and **11** (Scheme 5). Interestingly, treatment of **4** with a carbodiimide also results in a dichlorosilaimine **12** with the elimination of isonitrile.[36]

The upfield shift of the ^{29}Si NMR resonances for **10**–**12** (δ −99 to −100 ppm) with respect to **4** is due to higher coordinate silicon atoms and is consistent with Si(IV) compounds. The Si–N bond length of 1.56 Å in **12** (Figure 3) features a Si=N double bond character. An interesting feature is the shortening of the C–N bond of the imine moiety in **10**–**12**, which is probably due to the delocalization of the partial charge over the phenyl ring.

iii. Synthesis of a Dimer of Silaisonitrile. Organic nitriles and isonitriles are very stable, but their silicon analogues are transient species and only detectable in a low-temperature argon matrix.[37] The first transient silaisonitrile, HN=Si, was described in 1966 by Ogilvie and Cradock.[38] KC_8 reduction of **10** affords the cyclic silicon compound **13**[39] (Scheme 6). The proposed mechanism suggests the involvement of silaisonitrile **13**′ as an intermediate, which dimerizes to **13** with the elimination of free IPr. The silicon atoms in **13** are highly deshielded as shown by ^{29}Si NMR chemical shift at δ +183.29 ppm. Each of the silicon atoms in **13** is two-coordinate with a steroactive lone pair of electrons and this is the first base-free bis-silylene (Figure 4).[39]

SCHEME 4. Reactions of **4** with Ketones



7: R = Ph
8: R = 4-MeC$_6$H$_4$

9

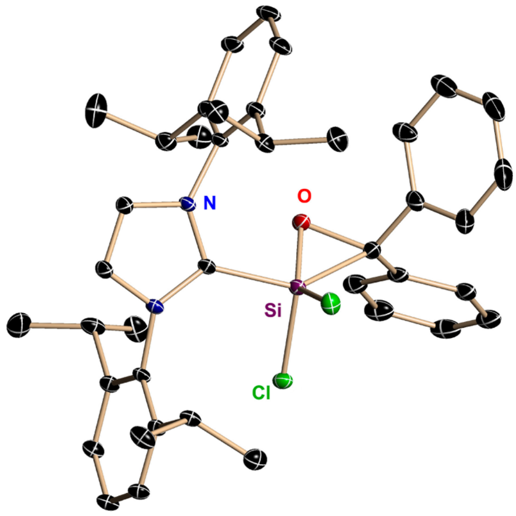
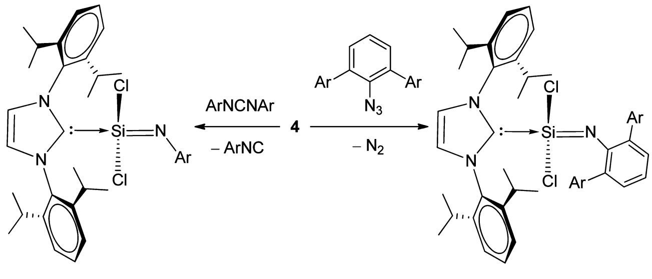


FIGURE 2. Molecular structure of **7**.

SCHEME 5. Synthesis of Dichlorosilaimines **10**−**12**



12: Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

10: Ar = 2,4,6-*i*Pr$_3$C$_6$H$_2$
11: Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

The calculated interatomic distances and angles of the model compound **13M** are in agreement with the experimental values of **13** (Figure 4). The elusive phenylisonitrile (PhNSi) is predicted with rather short C−N (1.371 Å) and N−Si (1.557 Å) bonds. The NICS values for **13M** of NICS(0) = 5.01 and NICS(1) = 0.91 support an antiaromatic character of the cyclic N$_2$Si$_2$ moiety.

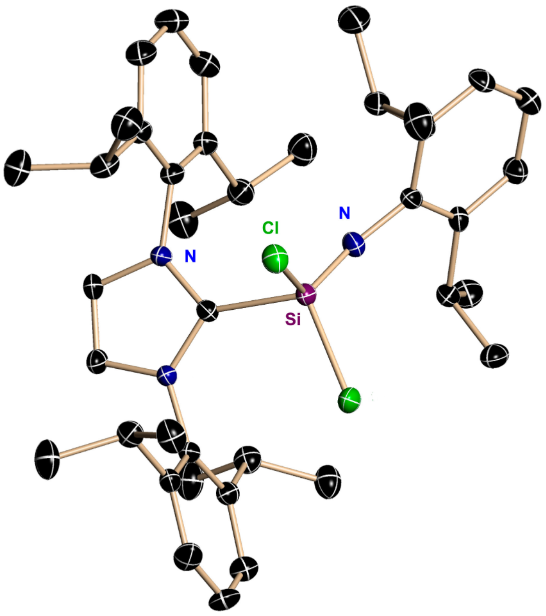


FIGURE 3. Molecular structure of **12**.

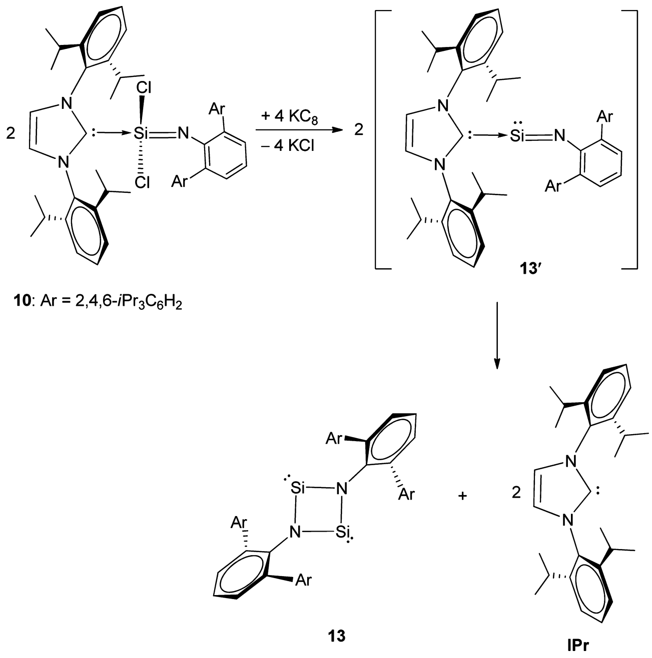
Only one base-free monosilaimine is known with a terphenyl group on the imine nitrogen atom.[40] Compound **13** is kinetically stabilized with bulky aryl groups on the nitrogen atoms. The lone pairs of the electrons on the silicon atoms are still available for further reaction as evidenced by its treatment with Me$_3$SiN$_3$ to yield the first base-free bis(silaimine) **14** (Scheme 7). Single crystal X-ray study supports the formation of **14** (Figure 5).

iv. Functionalization of NHC with (NHC)SiCl$_2$. Functionalization of NHCs at the C-4 and C-5 positions has attracted considerable attention as it alters the electronic properties of NHCs. Treatment of **4** with 1-azidoadamantane (AdN$_3$) affords C-4-silyl-substituted NHC **15** by oxidative addition and C−H activation (Scheme 8).[41] The proposed mechanism suggests the involvement of unstable silaimine **15′** under evolution of nitrogen gas. Silaimine **15′** consists of an easily polarizable Si=N bond and hence abstracts the proton from the C-4 position of the coordinated IPr ligand to form abnormal NHC **15**″, which rearranges to **15**. The observed imidazol geometry in **15** is very similar to that reported for free IPr (Figure 6).

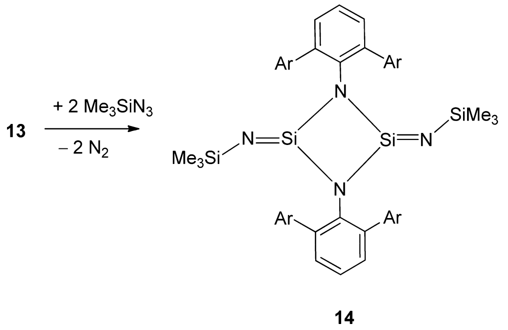
v. Reaction of 4 with Diphenylacetylene. Reaction of **4** with diphenylacetylene reveals that the NHC is labile enough to liberate the NHC and $SiCl_2$ species during the course of the reaction for generating derivative **16** (Scheme 9).[27] Compound **16** features three $SiCl_2$ moiety in a five-membered Si_3C_2 ring with four- and five-coordinate silicon atoms which are observed at δ −2.84 and −142.47 ppm in the ^{29}Si NMR spectrum (Figure 7).[27]

vi. Ambiphilicity of Dichlorosilylenes. The ambiphilicity of a silylene (**C** and **D**; Chart 3) has long been intriguing scientists during the last few decades, and a few silylene Lewis base adducts have been reported. In compound **4**, NHC is a Lewis base and $SiCl_2$ is a Lewis acid which possesses a lone pair of electrons. Therefore, **4** readily reacts with boranes to yield compounds **17** and **18**, in which $SiCl_2$

SCHEME 6. Reduction of Dichlorosilaimine **10** to Silaisonitrile Dimer **13**



SCHEME 7. Formation of Bis(silaimine) **14** with Three-Coordinate Silicon Atoms



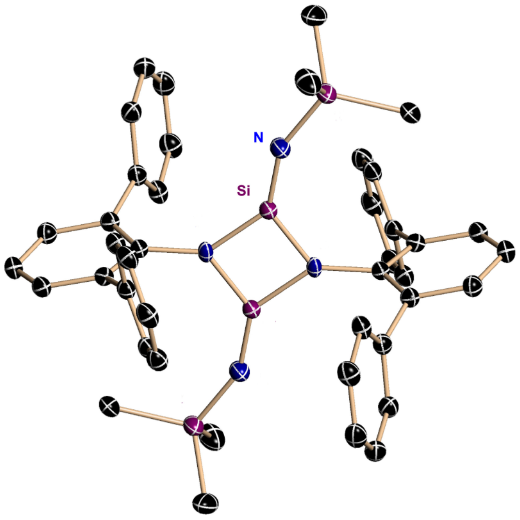


FIGURE 5. Molecular structure of **14**.

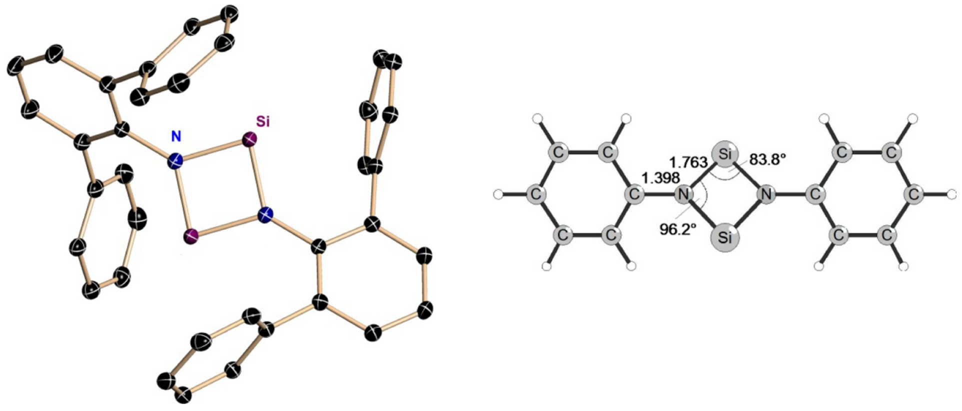


FIGURE 4. (left) Molecular structure of **13**; (right) calculated structure of the model compound of **13M**.

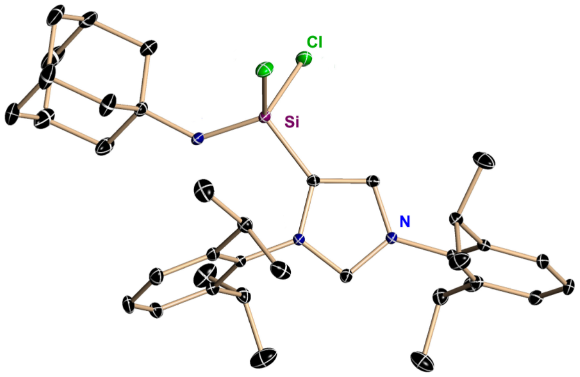
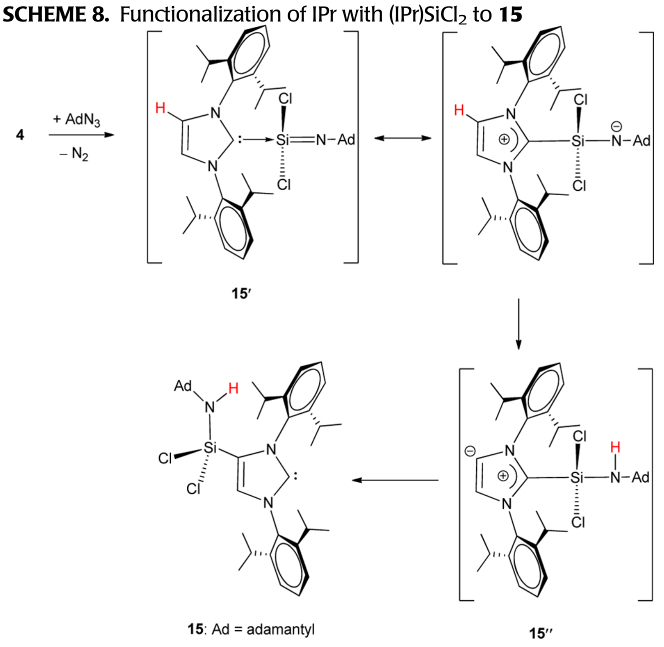
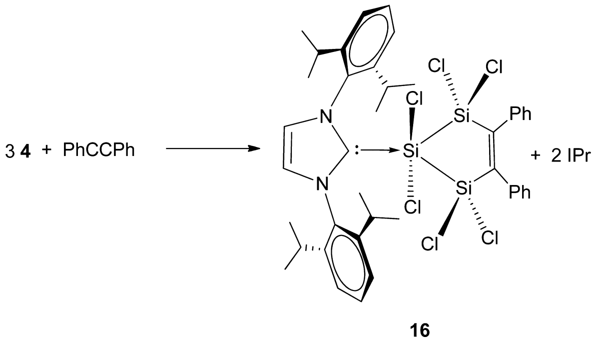


FIGURE 6. Molecular structure of **15**.

SCHEME 8. Functionalization of IPr with (IPr)SiCl$_2$ to **15**



SCHEME 9. Reactions of **4** with Diphenylacetylene to Trisilacyclopentene Derivative **16**



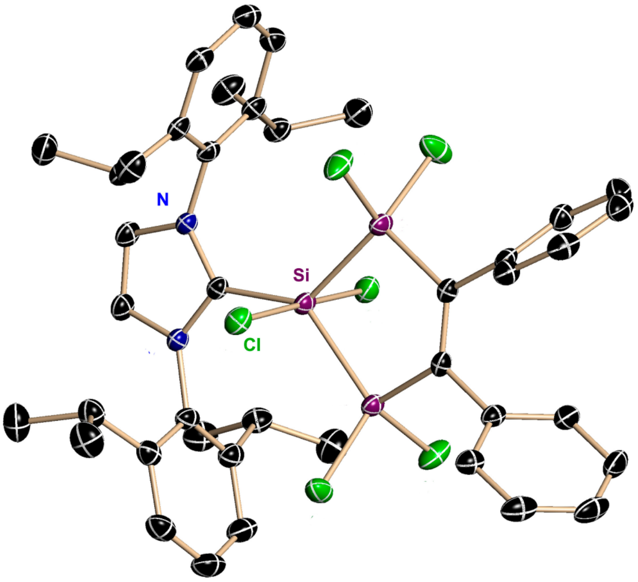
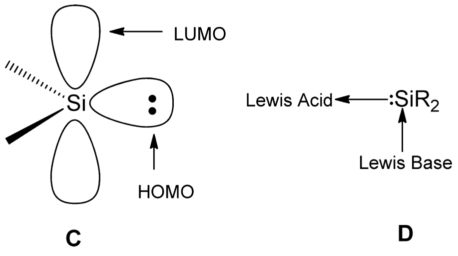


FIGURE 7. Molecular structure of **16**.

CHART 3. Ambiphilic Nature of a Silylene (:SiR$_2$)



functions as a Lewis acid as well as a Lewis base in a single molecule (Chart 3, Scheme 10).[42,43]

One of the representative compounds is shown in Figure 8. Both silicon and boron atoms are four-coordinate. The Si–Cl bond length (2.06 Å) in **17** is noticeably shorter than that in **4** (2.17 Å). The Si→B bond length is comparable with a Si–B single bond in silylboranes but larger than that observed in silaborene.

Compound **17** exhibits two interesting bonding modes (C→Si and Si→B) in the same molecule.[42] Both C→Si and Si→B donor bonds are confirmed by bond critical points (BCPs). The characteristics of a bond can be deduced by evaluating the density and its derivatives at the BCP. While the electron density at the BCPs in both cases is nearly identical (0.55 and 0.57 eÅ^{-3}), the Laplacians differ considerably (Figure 9). A negative Laplacian at the BCP is an indicator for predominantly covalent bonding and a positive Laplacian for predominantly polar or ionic bonding. Compared to the carbene, the silylene is a much softer donor because the BCP at the C→Si bond is located much closer to the silicon (0.77) than the BCP at the Si→B bond (1.26 Å).

vii. Dichlorosilylene as a Neutral σ-Donor Ligand for Transition Metal Complexes. Use of NHCs as σ-donor ligands in transition metal (TM) chemistry has received considerable attention,[44] particularly as alternatives to phosphines

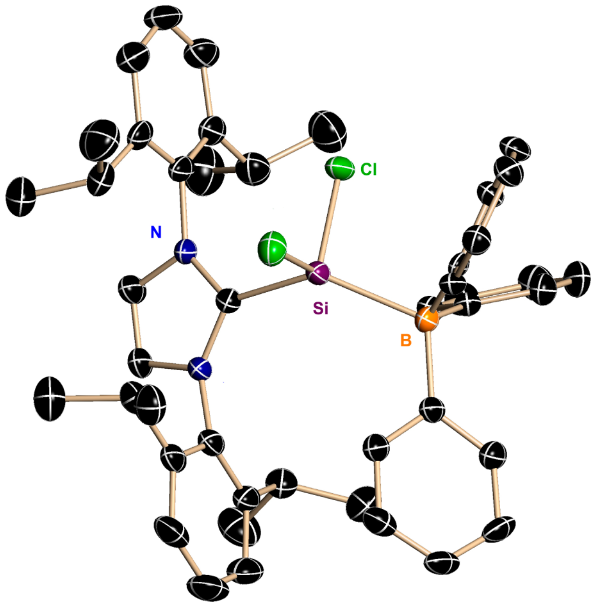
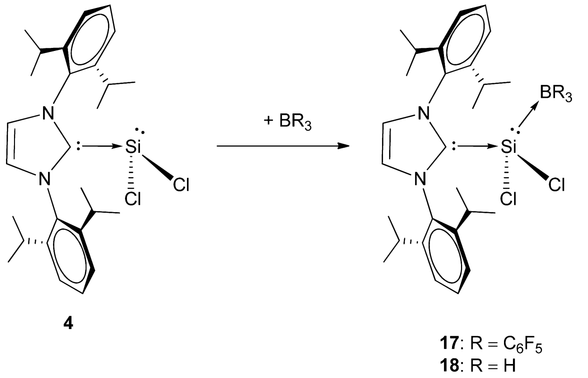


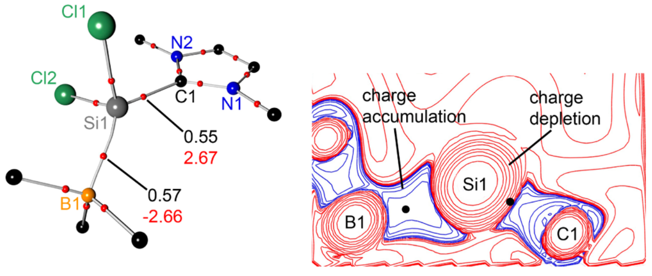
FIGURE 8. Molecular structure of **17**. F atoms are omitted for clarity.

SCHEME 10. Dichlorosilylene as a Lewis Acid and a Lewis Base in **17** and **18**



(R_3P), which led to a second generation of Grubbs catalysts.[44c] Silylene **4** reacts with a variety of TM-carbonyls to generate mono- or bis-silylene-TM complexes (Schemes 11 and 12).[45−48] Reaction of **4** with $Fe_2(CO)_9$, (η^5-C_5H_5)$Co(CO)_2$, and (η^5-C_5H_5)$V(CO)_4$ results in the 1:1 complexes of **19**, **20**, and **21**, respectively (Scheme 11).[45] Complex **21** is the first vanadium−silylene complex that was characterized by X-ray structural analysis. The short Fe−Si (2.22 Å), Co−Si (2.13 Å), and V−Si (2.40 Å) bond lengths of **19**, **20**, and **21** may be due to the π-back bonding (Figure 10).

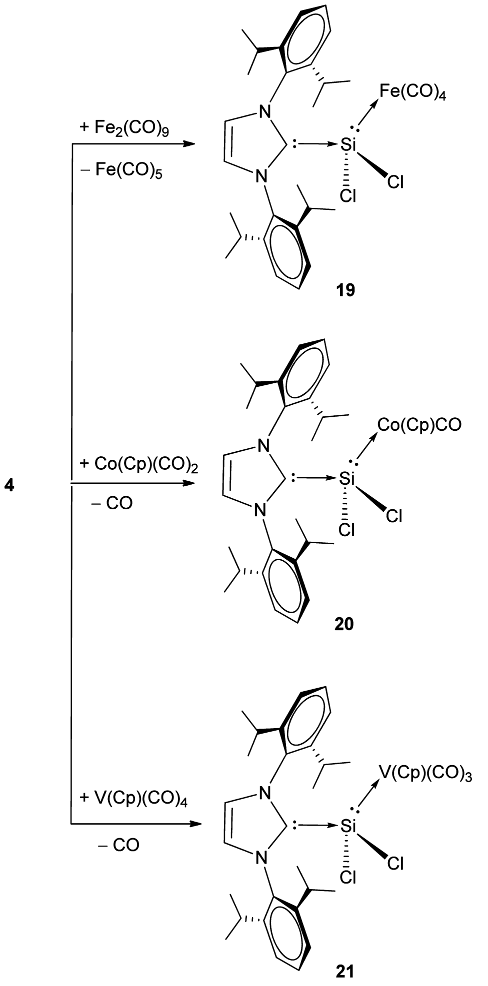
Treatment of **4** with $Ni(CO)_4$, $Co_2(CO)_8$, and $RhCl_2(CO)_2$ affords the bis-silylene-TM complexes **22**, **23**, and **24**, respectively (Scheme 12).[46−48] In **23**, compound **4** is a chlorinating and oxidizing agent.[47] The cation $[(\mathbf{4})_2Co(CO)_3]^+$ of **23** adopts a slightly distorted trigonal-bipyramidal geometry with an almost linear Si−Co−Si bond at the apical positions (Figure 11).



(a) (b)

FIGURE 9. (a) Molecular graph of compound **17** obtained from a gas phase optimization (B3LYP/TZVP). The small black spheres indicate BCPs, with $\rho(r_{BCP})$ [eÅ^{-3}] (upper number) and $\nabla^2\rho(r_{BCP})$ [eÅ^{-5}] (bottom number); and (b) contour plot of $\nabla^2\rho(r)$ (bottom) for the C1−Si1−B1 plane.

SCHEME 11. Monodichlorosilylene Transition Metal Complexes **19**−**21** (Cp = η^5-C_5H_5)



The THF solution of **23** exhibits two characteristic absorptions at 587 and 693 nm, which are ascribed to the *d*−*d* transition from the ground state $^4A_2$ to the $^4T_1$(P) state of the pseudotetrahedral cobalt(II) anionic moiety.

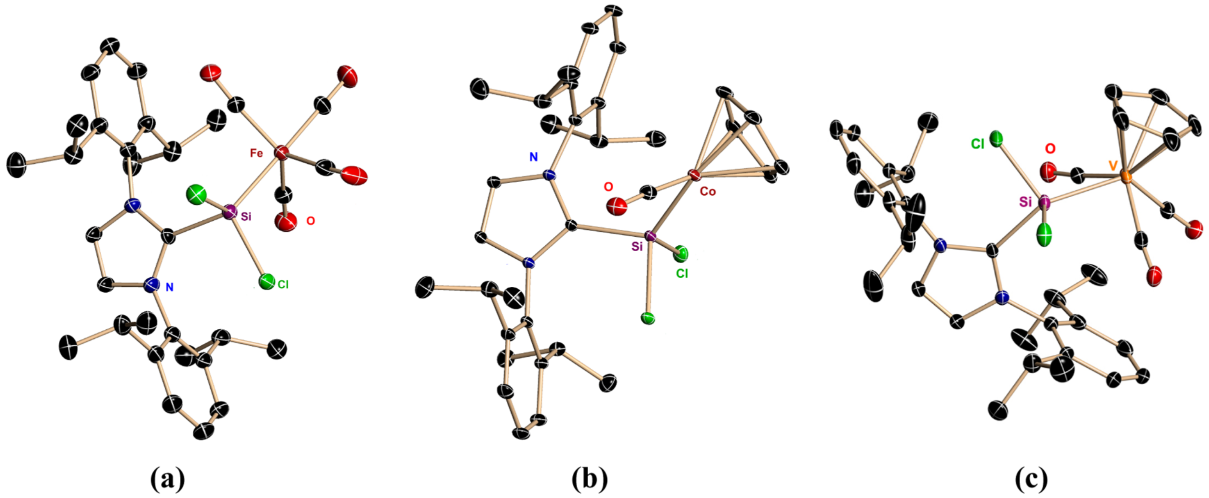
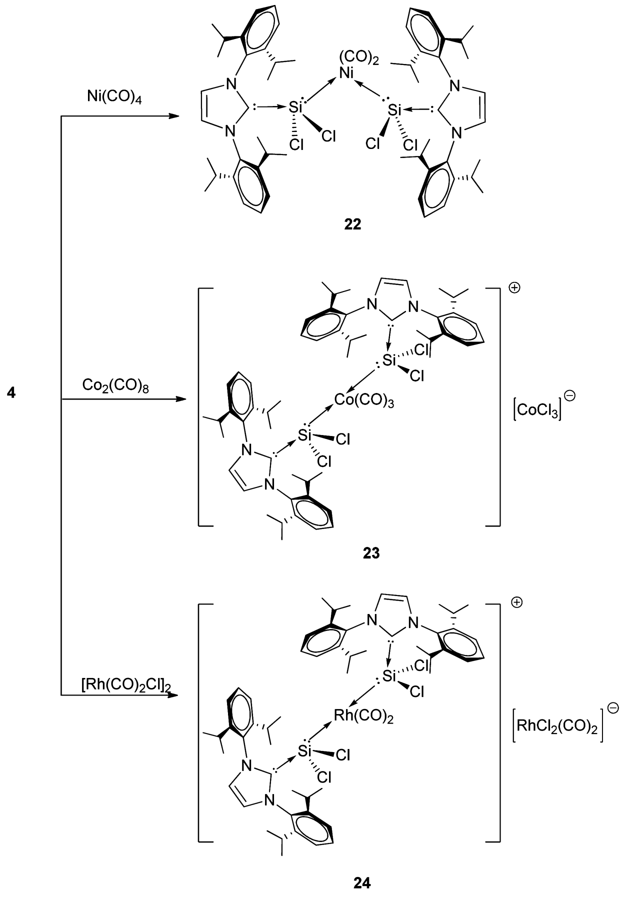


FIGURE 10. Molecular structures of **19** (**a**), **20** (**b**), and **21** (**c**).

SCHEME 12. Bis(dichlorosilylene) Transition Metal Complexes **22**–**24**



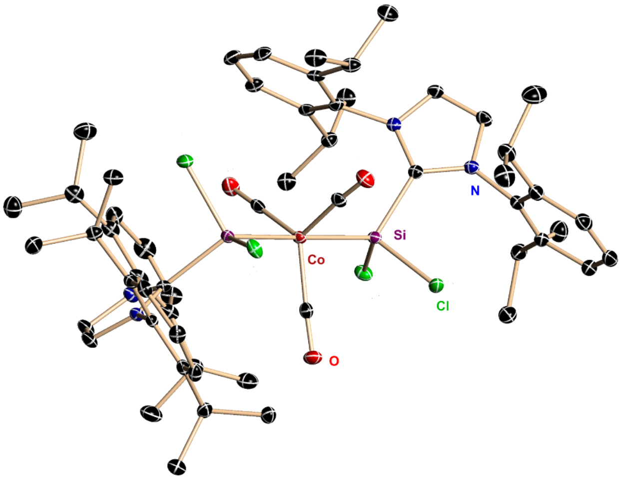


FIGURE 11. Molecular structure of the cationic part of **23**.

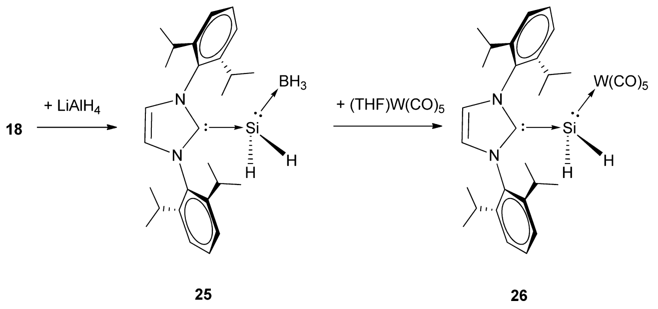
viii. Donor–Acceptor Stabilization of SiH_2. The existence of the silylene prototype SiH_2 has been postulated in the thermal decomposition of SiH_4 to form silicon.[49] The donor–acceptor stabilization of elusive reactive main group molecules has become an interesting breakthrough in recent research work. Rivard and co-workers reported[48] on the $LiAlH_4$ reduction of **18** to yield a donor–acceptor stabilized dihydrosilylene **25**. The Lewis acid BH_3 is labile and can be replaced with $W(CO)_5$ by treating **25** with $(THF)W(CO)_5$ to yield **26** (Scheme 13). The molecular structure of **26** is shown in Figure 12, which features a distorted tetrahedral geometry around the silicon atom.

ix. Synthesis of Silaallene and Higher Alkene Analogues (SiH_2EH_2, E = Ge or Sn). Reaction of **4** with $[(THF)ECl_2]W(CO)_5$ results in the formation of $[(\mathbf{4})ECl_2]W(CO)_5$ (E = Ge (**27**) and Sn (**28**)) with the elimination of THF[50] (Scheme 14). $LiAlH_4$ reduction of **27** and **28** affords a higher alkene analogue of **29** and **30**, respectively. Compounds **29** and **30** are isostructural (Figure 13). Both compounds **29** and **30** show considerable thermal stability in the solid state and decompose at ca. 135 °C. Treatment of **29** with acetylacetone results in the hydrosilylation reaction to afford **31** (Scheme 15).

x. Synthesis of Donor−Acceptor Stabilized Silaformylchloride. Formaldehyde ($H_2C{=}O$) is the simplest carbonyl compound and its monochlorinated derivative, formyl chloride **E** (Chart 4), is a useful formylating agent.[51] Interestingly, formyl chloride **E** is unstable at room temperature and decomposes to HCl and CO.[51] Isolation of a stable silicon analogue **F** of formyl chloride with a Si═O bond is evidently more challenging due to the instability of **E**. Reaction of **4** with $(H_2O)B(C_6F_5)_3$ in the presence of IPr affords a donor−acceptor stabilized silacarbonyl chloride **32** (Scheme 16).[52] The proposed mechanism suggests the initial formation of **32**′ as an intermediate on insertion of **4** at the H−O bond of water. Proton abstraction by IPr base with concomitant chloride elimination as insoluble (IPr)HCl to give **32** seems plausible. Compound **32** is not only the first acyclic silacarbonyl compound reported so far, but **32** is also the first stable halo-silacarbonyl compound. A broad resonance at δ 5.55 ppm is assigned for the Si*H* proton and supported by the $^1H-^{29}Si$ HSQC experiment.[52]

The molecular structure of **32** features a distorted tetrahedral geometry around the silicon atom (Figure 14). All four

SCHEME 13. Donor−Acceptor Stabilized Silicon(II) Dihydride of **25** and of **26**



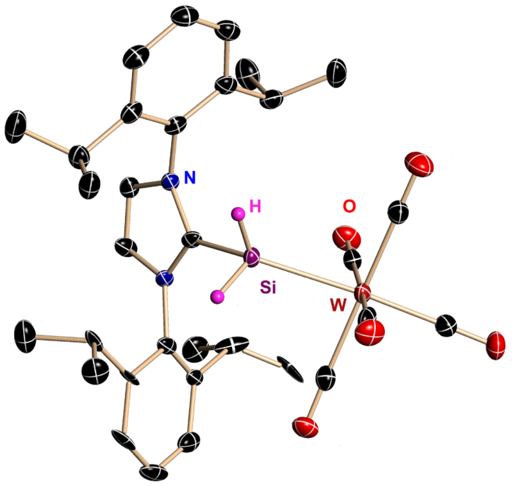


FIGURE 12. Molecular structure of **26**.

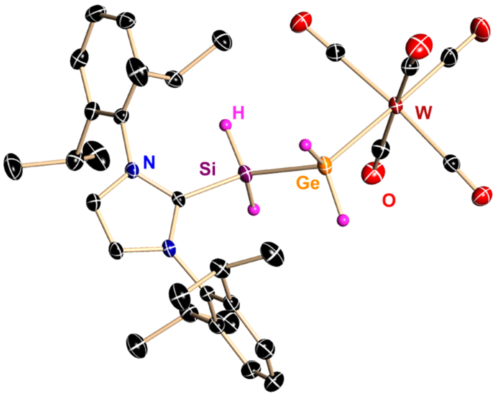
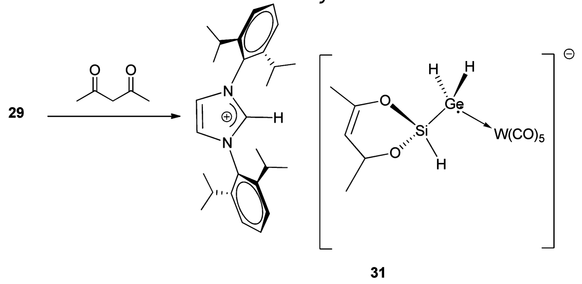


FIGURE 13. Molecular structure of **29**.

SCHEME 15. Reaction of **29** with acetylacetone to **31**



SCHEME 14. Synthesis of **27**−**30**

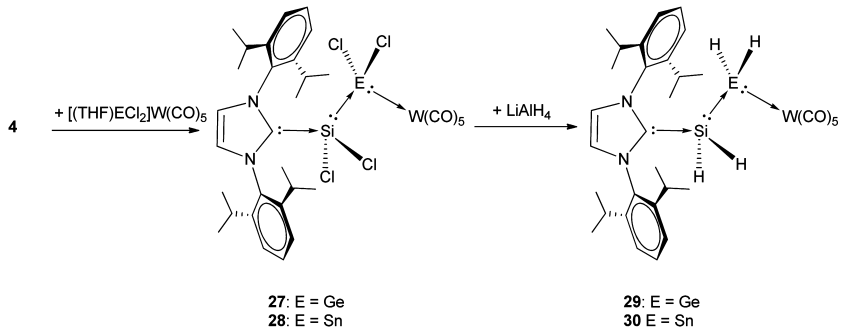
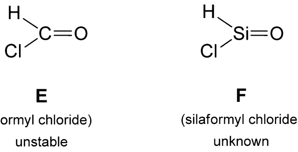
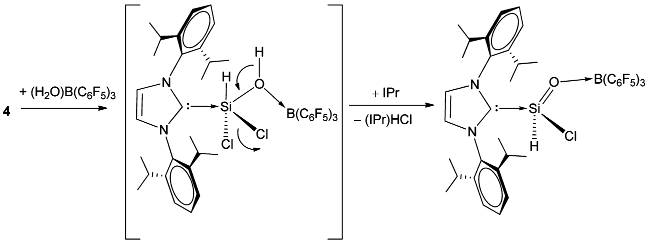


CHART 4. Formyl Chloride (**E**) and its Silicon Analogue (**F**)



SCHEME 16. Synthesis of Donor–Acceptor Stabilized Silaformyl Chloride **32**



32′ **32**

coordination sites are occupied by four different atoms (H, C, B, and O). The Si–O bond length (1.568(15) Å) is smaller than the Si–O single bond (1.64 Å) but longer than the Si=O bond calculated for $H_2Si{=}O$ (1.53 Å).

xi. Synthesis of Silaallene by Metathesis Reaction. Sekiguchi and co-workers reported tetrasilyl substituted trisilaallene **33** as red crystals by the reaction of **4** with dilithiosilane (Scheme 17).[53] The molecular structure of **33** features a bent Si–Si–Si angle of 164.3°, which was performed only by theoretical calculations.[53]

xii. Interaction of Dichlorosilylene with Muon. Among the physical methods for understanding the reactivity of silylene, μSR (muon spin resonance) spectroscopy is an important tool. The muonium (Mu) is a single-electron atom, the nucleus of which is the positive muon. Identification of the muoniated radicals formed by Mu addition to a silylene provides clear evidence of its reactivity. Muon irradiation of a THF solution of **4** resulted in a single muoniated radical (**4**+Mu) formation (Scheme 18) as evident from the μSR spectrum.[54] The μSR spectrum of **4**+Mu shows three resonances, two of which are due to the two chlorine isotopes. Computational study of the possible adducts of **4** reveals that H addition to the silicon is favored over addition to the carbene by 62 kJ mol^{-1}.

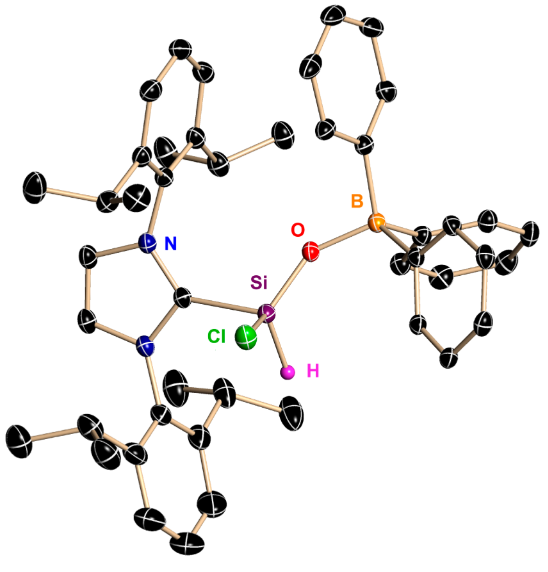
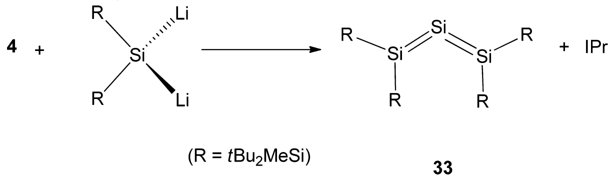


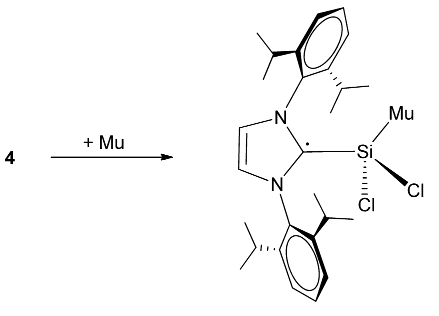
FIGURE 14. Molecular structure of **32**.

SCHEME 17. Synthesis Tris-silaallene **33**



33

SCHEME 18. Interaction of **4** with Muon



4 + Mu

4. Summary and Future Prospects

Synthesis, properties, and reactivity of dichlorosilylenes (NHC)$SiCl_2$ have been presented. The dichlorosilylenes are prepared in high yield following a very facile method that requires safe reducing agents. The facile access to monosilicon epoxides and silaisonitrile, and their structural characterization have been presented providing experimental data for further theoretical investigations and their comparison with carbon analogues. The stability of silaimine formed by the reaction of dichlorosilylene with organic azide highly depends on the organic substituents. KC_8 reduction of dichlorosilaimine affords a dimer of silaisonitrile with a two-coordinate silicon atom and can be regarded as a bis(silylene). This is a four π-electron antiaromate, which is very uncommon in silicon chemistry. Therefore, reactivity study of this novel compound is highly desirable. The first bis(silaimine) with three-coordinate silicon atoms has also been reported. The exploration of chemistry of $(NHC)SiCl_2$ is still in its infancy, and there is a huge potential of this system to generate interesting silicon compounds. The availability of a facile high yield method for dichlorosilylenes **4** and **5** will hopefully facilitate a rapid development of organosilicon compounds with low-valent silicon. The chemistry and ligand properties of these species are encouraging not only for synthetic chemists but also for materials scientists.

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BIOGRAPHICAL INFORMATION

Rajendra S. Ghadwal studied chemistry at the University of Rajasthan Jaipur and obtained his M.Sc. degree in 2000. He then worked as a Lecturer until 2002. He began his doctoral research under the supervision of (late) Prof. R. C. Mehrotra and Prof. Anirudh Singh and received his Ph.D. degree in 2006. In 2008 he joined the research group of Prof. Herbert W. Roesky at the Georg-August-Universität Göttingen as a postdoctoral researcher. His postdoctoral work was focused on stable singlet carbene stabilized silylenes and silicon−heteroatom multiple bonded compounds. Following his postdoctoral tenure, he started independent research at the Georg-August-Universität Göttingen in 2011. His current research interests include molecular chemistry of transition and main group elements in low-oxidation state, particularly multiply bonded compounds and metal hydrides and their application in small molecules activation and homogeneous catalysis. Dr. Ghadwal has published more than 35 research papers.

Ramachandran Azhakar obtained his Ph.D. (Indian Institute of Technology − Kanpur, India) in 2006. After completion of his doctoral research with Prof. Vadapalli Chandrasekhar, he received a Japan Society for the Promotion of Science postdoctoral fellowship to do research at Kyoto University, Japan in the group of Prof. Susumu Kitagawa. In 2009 he joined the research group of Prof. Herbert W. Roesky at the Georg-August-Universität Göttingen, Germany, as an Alexander von Humboldt postdoctoral fellow. His research interest lies in the area of transition metals and main group elements. He is currently focused on chemistry of compounds with low-valent silicon. He has coauthored around 45 research papers in peer reviewed international journals.

Herbert W. Roesky obtained his doctorate from Georg-August-Universität Göttingen. After working at Du Pont in the United States, he returned to Göttingen and finished his habilitation. Then he became a professor at the Johann-Wolfgang-Goethe-Universität, Frankfurt am Main in 1971. He moved to Georg-August-Universität Göttingen in 1980 and was the director of the Institute for Inorganic Chemistry until 2004. He is primarily known for his pioneering work on fluorides of both transition and main group elements. His current research interest is focused on the synthesis and reactivity of compounds with heavier group 13 and 14 elements in low oxidation states. More than 1200 peer-reviewed papers, articles, patents, and books record his research activity in the areas of Inorganic Chemistry and Material sciences.

FOOTNOTES

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The authors declare no competing financial interest.

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