

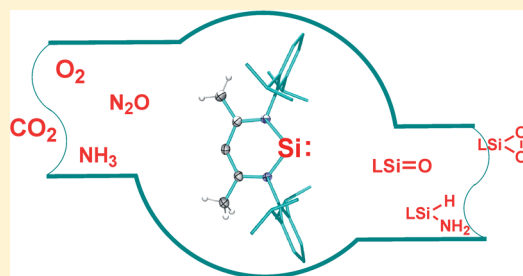
Zwitterionic and Donor-Stabilized N-Heterocyclic Silylenes (NHSis) for Metal-Free Activation of Small Molecules[†]

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Supporting Information

ABSTRACT: This account describes recent progress (>2006) in the synthesis and structural characterization of isolable N-heterocyclic silylenes (NHSis) and their fascinating reactivities with respect to an emergent topic in main-group chemistry: metal-free small-molecule activation. Since the seminal discovery of stable N-heterocyclic silicon analogues of nucleophilic Wanzlick–Arduengo-type carbenes in 1994, new types of NHSis have emerged with unique electronic features and strikingly different reactivities. Among them, the first zwitterionic (ylide-like) silylene LSi: ($\text{L} = \text{CH}[(\text{C}=\text{CH}_2)\text{CMe}][\text{NAr}]_2$; $\text{Ar} = 2,6\text{-Pr}^t_2\text{C}_6\text{H}_3$) and unprecedented N-heterocyclic bis(silylenes) with amidinate ligands and $\text{Si(I)}\text{--Si(I)}$ bonds were synthesized. Their striking electronic structures open new doorways to metal-free activation of C--H , C--X , Si--X , E--H ($\text{E} = \text{group 15, group 16 elements}$), P--P , E--O ($\text{E} = \text{C, N}$), and E--E bonds ($\text{E} = \text{O, S, Se, Te}$).



1. INTRODUCTION

Silylenes are divalent, dicoordinate neutral silicon species. They are highly reactive and represent indispensable building blocks for the synthesis of value-added organosilanes through oxidative addition and small-molecule activation.¹ As heavier analogues of carbenes, silylenes generally possess a singlet ground state, due to the large energy gap and spatial difference between the silicon 3s and 3p orbitals.² A remarkable exception is bis(tri-*tert*-butylsilyl)silylene, which has a triplet ground state, as indicated by EPR spectroscopy and computational studies.³ Until two decades ago, silylenes have been considered to be extremely elusive species which undergo conversion even at low temperature ($>-196\text{ }^\circ\text{C}$).⁴ However, this situation changed profoundly in 1994, when Denk, West, et al. described the synthesis of the first isolable N-heterocyclic silylenes **Ia** (Chart 1) by reducing the corresponding N-heterocyclic silicon(IV) dichloride precursor with elemental potassium.⁵ Recently, the two aryl-supported versions **Ib,c** of this type of stable silylene were reported.⁶ The latter systems with unsaturated chelating ligands benefit from π -donor stabilization of the low-valent silicon(II) atom by both nitrogen atoms and pseudoaromaticity as well as steric protection through bulky organic groups. In comparison with silylenes **Ia–c**, the substituted saturated silylenes **IIa–e**,^{7–9} which have also been synthesized and isolated, are less stable. For instance, **IIa** is stable in dilute solutions; however, in concentrated solution or in the solid state, it undergoes reversible tetramerization.¹⁰ Interestingly, such oligomerization has not been observed for silylenes **IIb–e**. The third group of stable silylenes is type **III**, with a benzo-fused five-membered-ring system, including the unique example of a bis-silylene **IIIId**, reported by Lappert and co-workers.^{11–13} During the last two

decades, the chemistry of N-heterocyclic silylenes of types **I–III** has been well developed and documented.¹⁴ In contrast, silylenes without N-heterocyclic donor stabilization are generally considered as labile species. Likewise, acyclic silylene **IV**, which has recently been examined, exists only below $0\text{ }^\circ\text{C}$.¹⁵ Remarkably, the unsupported dialkylsilylene **V** had also been isolated by Kira et al. Although the latter is kinetically stabilized, it isomerizes slowly to a cyclic silene at ambient temperature in solution.¹⁶ The interesting chemistry of this species has also been summarized in review articles.¹⁷ In contrast, the decamethylcyclopentadienyl-supported Si(II) species **VI** is quite stable and has been known since 1986. Its rich chemistry has also been well documented.¹⁸

Our entry into this field started in 2006 with the discovery of the stable N-heterocyclic silylene **1** (Chart 2) bearing a modified β -diketiminato ligand.¹⁹ Due to the ylide-like electronic resonance structures **1'** and **1''**, the chemistry of silylene **1** is distinctly different from that of the isolable silylenes mentioned above. The exocyclic methylene group, which may behave as an additional nucleophilic group, cooperates with the two reactive sites (a lone pair and an empty 3p orbital) of the silicon(II) center and makes this species multifunctional toward both electrophiles and nucleophiles. In fact, shortly after the synthesis of **1**, its wide-ranging chemistry, especially its capability of activating small molecules, attracted considerable attention. Accordingly, the reaction of H_2O with **1** led to the mixed-valent siloxy silylene **2** (Chart 2).²⁰ The latter species is an intramolecular donor-stabilized silylene and represents the first silicon(II) complex supported by a β -diketiminato ligand. Owing to the intramolecular $\text{N(imine)}\rightarrow\text{Si(II)}$ coordination,

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Chart 1

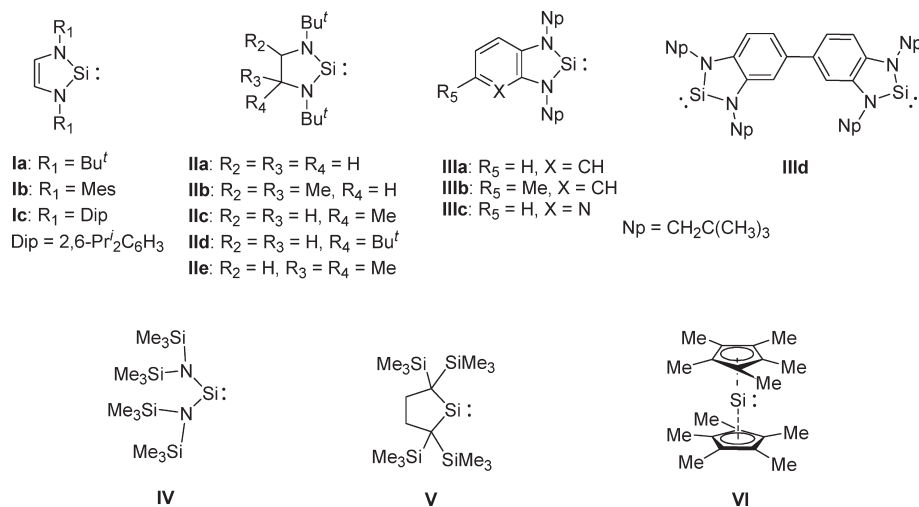
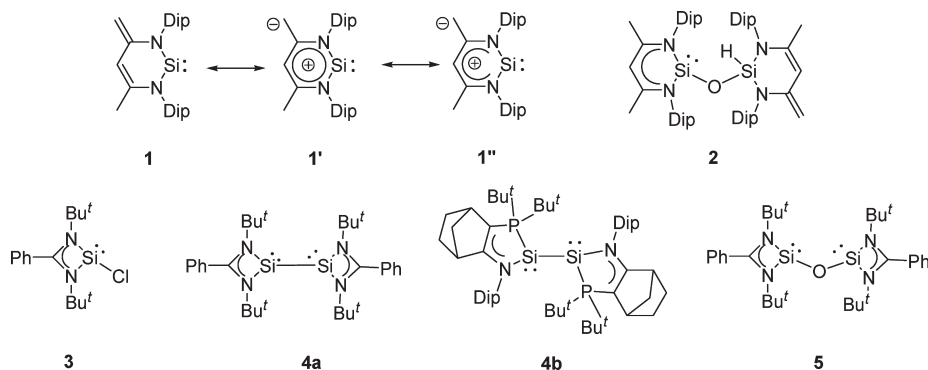


Chart 2



compound **2** is remarkably nucleophilic and capable of activating small molecules such as N_2O and CO_2 to form the corresponding silanoic silyl ester via oxygen transfer to Si(II).²¹ Such metal-free bond activation has recently become an active area of research.²² In 2006, the similar intramolecular donor-stabilized NHSi **3** with a terminal Si(II)—Cl bond and supported by amidinate was reported by Roesky and co-workers.²³ The latter exhibits quite a rich chemistry. Shortly after the discovery of **3**, the bis-NHSi's **4a,b** were prepared by Roesky et al.²⁴ and Baceiredo et al.,²⁵ respectively. Featuring a Si(I)—Si(I) bond, compounds **4a,b** show unprecedented and versatile reactivities with respect to small-molecule activation. Very recently, the novel bis-NHSi **5** was synthesized by our group.²⁶

Since several comprehensive reviews have been published on the synthesis and reactivity of isolable silylenes,^{14,17} especially of types I—III and V, this survey deals solely with the synthesis and structures of **1**—**3** and their striking reactivities with the main emphasis on small-molecule activation. In addition, the synthesis and reactivities of the unique bis-NHSi's **4a,b** and **5** are included.

2. SYNTHESIS AND CHARACTERIZATION OF NEW TYPES OF NHSI'S

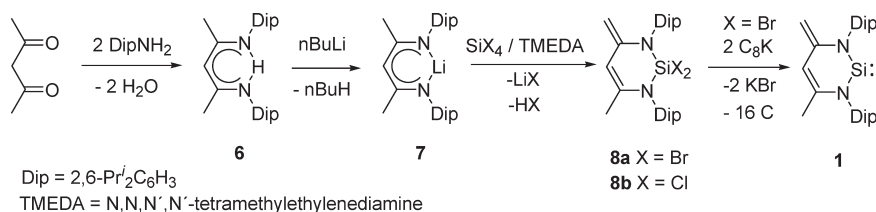
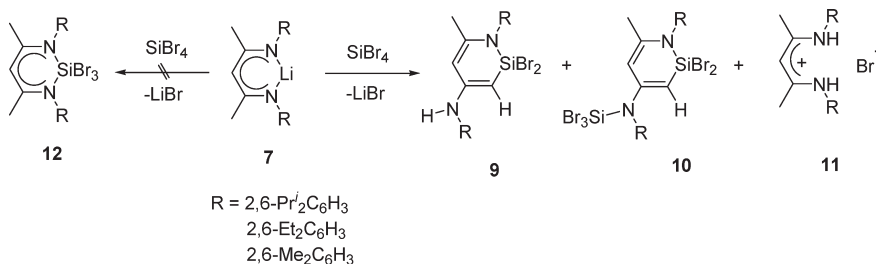
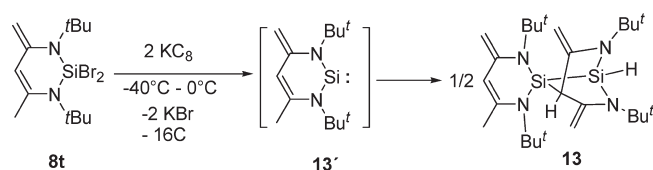
2.1. Zwitterionic (Ylide-Like) Silylene 1. The synthesis of NHSi **1**, based on the β -diketiminato ligand **6** and via the

dibromosilane precursor **8a**, is shown in Scheme 1.¹⁹ Ligand **6** is easily accessible by a straightforward protocol in ca. 70% yield.²⁷ The silylene precursor **8a** can also be prepared in high yield in a one-pot reaction by lithiation of **6** with *n*-BuLi or MeLi in diethyl ether to give **7**²⁸ and subsequent silylation with silicon tetrabromide in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA).

Using TMEDA as an auxiliary base for deprotonation at an exocyclic methyl group on the backbone of the ligand is crucial for the preparation of dibromosilane **8a**. In contrast, the reaction of lithiated ligand **7** with SiBr_4 in the absence of TMEDA led to the formation of different types of *N*-heterocyclic dibromosilanes, namely **9** and **10**, instead of **8a** along with byproduct **11** (Scheme 2).²⁹ Interestingly, the expected tribromosilane **12** could not be observed in the latter reaction. Starting from dibromosilane **8a**, the reduction with potassium graphite in tetrahydrofuran (THF) furnished the yellow silylene **1** after workup and crystallization in good yields (>75%) (Scheme 1).

The substitutions at both nitrogen atoms in **1** appear to be of great importance, because even analogues with slightly less bulky protecting groups did not lead to stable silylenes. For instance, debromination of the dibromosilane analogues of **8a** with 2,6-diethylphenyl or 2,6-dimethylphenyl groups at both nitrogen

Scheme 1. Synthesis of NHSi 1

Scheme 2. Reaction of Lithium β -Diketiminato 7 with SiBr_4 Scheme 3. Debromination of 8t with KC_8 

atoms was unsuccessful and led to an inseparable mixture. In the case of the *tert*-butyl version, the reduction of dibromosilane 8t with potassium graphite in THF yielded only the N-heterobicyclic disilane 13, a formal dimer of the desired zwitterionic silylene 13' (Scheme 3).³⁰

Moreover, although the dichloride analogue 8b can also be readily prepared by the same route used for 8a, its reduction does not lead to silylene 1. In fact, the reduction conditions are also crucial for the preparation of silylene 1. For instance, elemental potassium has been tested and silylene 1 did form as the main product, but the reaction is much slower than that using potassium graphite. On the other hand, excess amounts of potassium graphite should be avoided, as over-reduction might occur, leading to undesired products.

NHSi 1 has been fully characterized by ^1H , ^{13}C , and ^{29}Si NMR spectroscopic, mass spectrometric, and elemental analyses as well as single-crystal X-ray crystallography.¹⁹ The last analysis revealed that 1 consists of a planar six-membered SiN_2C_3 ring with alternating endocyclic C–C distances of 1.402(2) Å (C2–C3) and 1.389(2) Å (C3–C4) and an exocyclic C2–C1 double bond (1.412(2) Å), respectively (Figure 1). Additionally, the remarkably short exocyclic C4–C5 single-bond distance of 1.436(2) Å reflects that the C–C bond length equilibration in the backbone is probably a shallow mode. This is confirmed by density functional theory (DFT, B3LYP/TZVP) calculations of the model compound, in which the 2,6-diisopropylphenyl groups at nitrogen have been replaced by 2,6-dimethylphenyl substituents.¹⁹ The calculations of magnetic properties of the latter model suggest a preference for

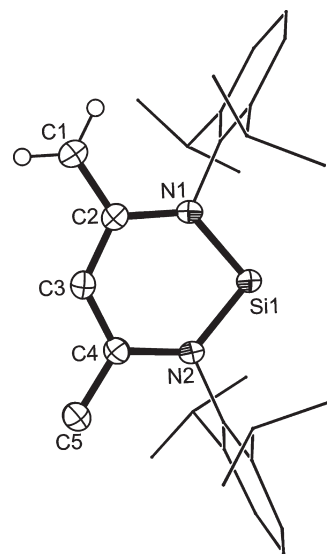


Figure 1. Molecular structure of 1 with thermal ellipsoids drawn at the 50% probability level. The H atoms, except those at C1, are omitted for clarity.

the mesomeric form 1'' (SiN_2 allyl-like form) over 1' (six- π -electron heterofulvene ylide form) (Chart 2), as indicated by the positive NICS values (NICS(0) = 3.6, NICS(1) = 1.4 ppm). The dipole moment calculation (DFT, B3LYP/6-311G) of 1 amounts to 1.8 D. Together with the theoretically calculated proton affinity of 1 (1099 kJ mol^{-1}) due to the exocyclic methylene group, an ylide-like character was suggested for this silylene.

The solid-state $^{29}\text{Si}\{^1\text{H}\}$ CP NMR spectrum of 1 recorded at a MAS frequency of 12 kHz exhibits a single sharp resonance at δ 88 ppm accompanied by spinning sidebands at a distance of 12 kHz from the resonance (Figure 2).³¹ The isotropic chemical shift of δ 88 ppm in the solid-state $^{29}\text{Si}\{^1\text{H}\}$ CP NMR spectrum of 1 is identical with the corresponding ^{29}Si chemical shift observed in benzene- d_6 solutions (δ 88.4 ppm). Thus, the isotropic ^{29}Si

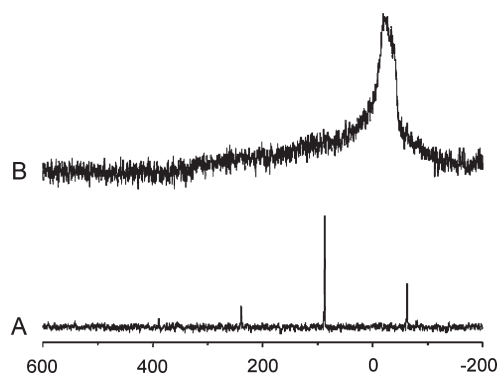
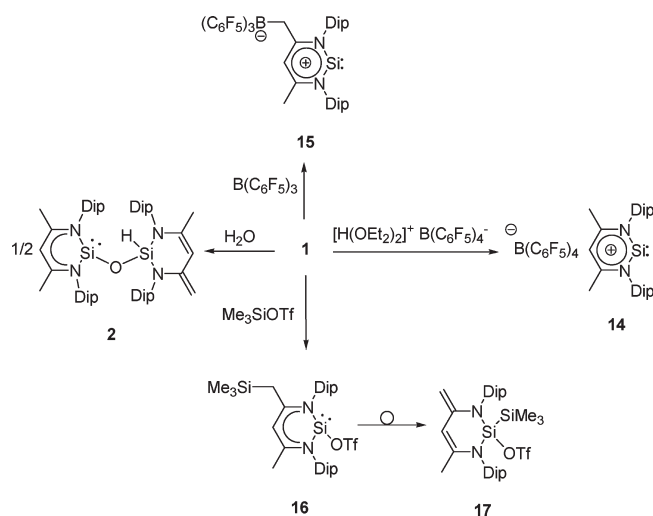


Figure 2. Solid-state $^{29}\text{Si}\{^1\text{H}\}$ CP NMR spectra of silylene **1** under (A) MAS conditions with a spinning frequency of 12 kHz and (B) static conditions. Chemical shift tensor: δ_{iso} 88, δ_{11} 320, δ_{22} -15, δ_{33} -63 ppm.

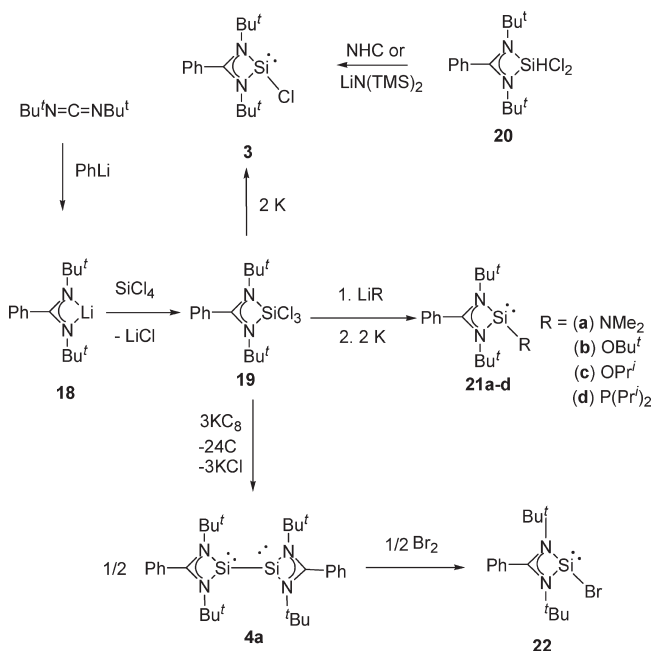
Scheme 4. Nucleophilic Reactions of **1** and the Formation of **2**



chemical shift of **1** is predominately determined by the electronic structure of a distinct silylene molecule, since there are no visible intermolecular effects on the ^{29}Si chemical shift. The latter chemical shifts are quite close to those of the N-heterocyclic, $p\pi-p\pi$ -conjugated silylenes **I** and **III** (δ 78.3–97.7 ppm), suggesting a similar electronic situation.³²

Due to the charge-separated resonance structures **1'** and **1''**, which emphasize that there are two possible nucleophilic centers, namely the nucleophilic silicon(II) center (lone pair electrons) and the exocyclic methylene group, in the system (Chart 2), the chemistry of silylene **1** is distinctively different from that of other known stable silylenes. Accordingly, the exocyclic nucleophilic site gives access to the novel cationic silylene (silylidenium) **14** by protonation of **1** with $[\text{H}(\text{OEt}_2)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (Scheme 4).^{33,34} Compound **14** represents a HSi^+ derivative with a two-coordinate Si^{II} atom ($\lambda^2\text{-Si}^{\text{II}}$) stabilized by N-chelate coordination and a planar (Hückel-like, 2D) aromatic six- π -electron delocalization. Remarkably, the intriguing “half-sandwich” cationic compound $[(\eta^5\text{-C}_5\text{Me}_5)\text{Si}]^+$ has been reported by Jutzi and co-workers.³⁵ The latter can be described as a three-dimensional (3D) aromatic species according to the Jemmis–Schleyer interstitial electron rule for “half-sandwich” (nido cluster) species.³⁶

Scheme 5. Synthesis of Chlorosilylene **3** and the Bis-NHSi **4a**



Moreover, treatment of the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ with **1** led to the formation of the zwitterionic NHSi–borane adduct **15**.³³ Nevertheless, the generalization that electrophiles react exclusively at the exocyclic methylene group cannot be made. In fact, upon addition of TMS-OTf ($\text{TMS} = \text{SiMe}_3$, $\text{OTf} = \text{OSO}_2\text{CF}_3$) to **1**, the silyl group does add to the methylene group while the OTf coordinates to the silicon center to give **16**; however, this 1,4-addition product is unstable and slowly undergoes isomerization to the 1,1-adduct **17** over the course of several days at room temperature.¹⁹ The latter observation is in agreement with the results of DFT calculations, which indicate that these two species are kinetic and thermodynamic products, respectively. Notably, the germanium analogue of **1** also reacts readily with TMS-OTf , giving only the 1,4-addition product owing to the lower basicity of $\text{Ge}(\text{II})$ lone pair electrons (inert-pair effect).³⁷

2.2. Synthesis and Structure of Mixed-Valent Disiloxane **2**

The unexpected siloxy silylene **2** results from exposure of solutions of **1** to very small concentrations of water. This has been managed by slow diffusion of water vapor into a hexane solution of **1** at 4 °C (Scheme 5),²⁰ whereby **2** crystallizes as brown-red crystals directly from the reaction solution. Compound **2** can be regarded as a mixed-valent disiloxane with one $\text{Si}(\text{IV})$ and one $\text{Si}(\text{II})$ center bridged by an oxygen atom. Remarkably, due to the presence of a tetracoordinate Si atom as a chiral center and hindered rotation around the Si-O bonds, **2** possesses two rotational isomers. Thus, the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum shows two singlet resonance signals at δ -7.9 and -9.6 ppm assignable to the silylene-like subunits and two doublet signals at δ -53.7 and -54.2 ppm ($^1J_{\text{HSi}} = 273$ Hz) for the siloxy ^{29}Si nuclei, respectively. Luckily, one of the two isomeric forms could be characterized structurally by X-ray diffraction analysis. Accordingly, the two almost planar $\text{C}_3\text{N}_2\text{Si}$ rings in **2** prefer a gauche conformation to each other (Figure 3). The silylene-like center adopts a trigonal-pyramidal geometry with a stereoactive lone pair of electrons. Although the $\text{Si}(\text{II})$ center is well protected

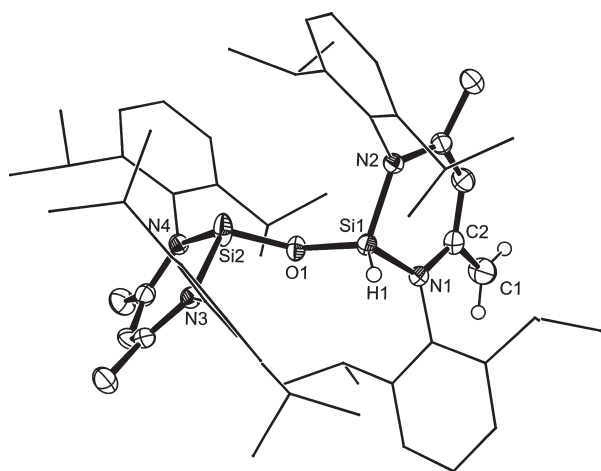


Figure 3. Molecular structure of **2** with thermal ellipsoids drawn at the 50% probability level. The H atoms, except those at Si1 and C1, are omitted for clarity.

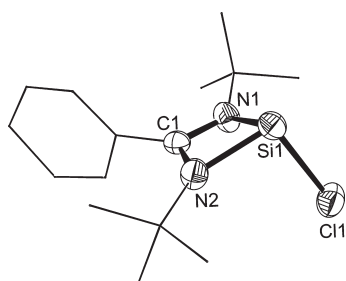


Figure 4. Molecular structure of **3** with thermal ellipsoids drawn at the 50% probability level.

by nearby isopropyl groups, it is remarkably reactive even toward marginally oxygenating molecules such as N_2O and CO_2 (see section 3).²¹

2.3. Synthesis and Characterization of Chlorosilylene 3.

The cyclic imine-stabilized chlorosilylene **3** was reported by Roesky and co-workers in 2006.³⁸ It was first synthesized by reduction of the trichloride precursor **19**, which results from the reaction of *tert*-butylcarbodiimide with 1 equiv of PhLi followed by treatment with SiCl_4 (Scheme 5). The yield of **3** by this protocol was moderate (ca. 10%). Very recently, two facile and improved syntheses of this compound were developed by the same group. Accordingly, **3** is readily accessible from the dichlorosilane precursor **20** by using an N-heterocyclic carbene (NHC) or $\text{LiN}(\text{TMS})_2$ as a Brønsted base in 35 or 90% yield, respectively.³⁹

The chlorosilylene **3** resonates at δ 14.6 ppm in the ^{29}Si NMR, showing an upfield shift relative to those of siloxy silylene **2** and those of homoleptic NHSi's. Its molecular structure, established by an X-ray diffraction analysis, revealed a puckered four-membered CN_2Si ring with a tricoordinate Si(II) center (Figure 4). Similar to the case for **2**, the silicon atom possesses a pyramidal geometry with a stereoactive lone pair of electrons, which accounts for the reactivity. Theoretical calculations have also been done to reveal the bonding situation in **3**.⁴¹

Since only one derivative with a *N-tert*-butyl and ring C-phenyl substitution pattern could be isolated at this point, the substituents at both nitrogens and the ring carbon seem to play an important role. On the other hand, one Cl atom of the trichloride **19** could be easily replaced by amido, alkoxido, and phosphido

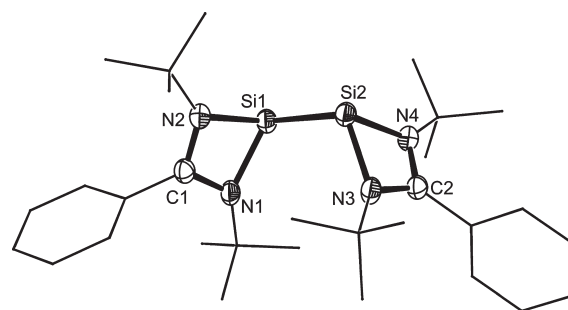
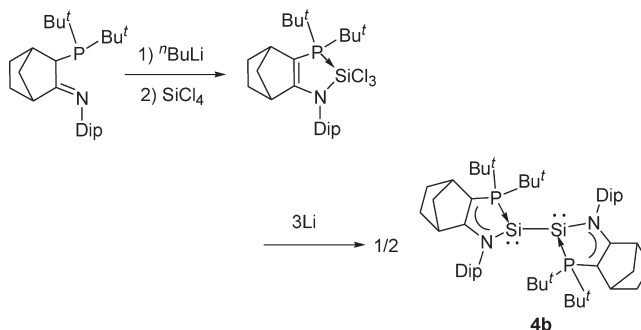


Figure 5. Molecular structure of **4a** with thermal ellipsoids drawn at the 50% probability level.

Scheme 6. Synthesis of the Bis-NHSi **4b**



groups, respectively, and subsequent reduction of such species with elemental potassium led to the corresponding heteroleptic NHSi's **21a–d** in reasonable yields (41–52%).⁴⁰

2.4. Synthesis and Characterization of the Bis-NHSi's **4a,b**.

Remarkably, the reduction of trichlorosilane **19** with 3 equiv of potassium graphite furnished bis(silylene) **4a**. The product was isolated in low yield (5.2%) as orange-red crystals from the resulting mixture (Scheme 5).⁴¹ With a formal oxidation state of +I, the silicon atom in **4a** shows a resonance at δ 75.7 ppm in the ^{29}Si NMR spectrum, which is downfield compared to that of the NHC donor-stabilized $\text{NHC} \rightarrow \text{Si}(\text{Cl})\text{Si}(\text{Cl}) \leftarrow \text{NHC}$ complex (38.4 ppm) reported by Robinson et al.⁴² It is noteworthy that the ^{29}Si chemical shift of **4a** is comparable to the value reported for the isolable disilyne $\text{RSi} \equiv \text{SiR}$ (89 ppm; $\text{R} = \text{Si}(\text{Pr}^i)\{\text{CH}[\text{SiMe}_3]_2\}_2$) described by Sekiguchi and co-workers.⁴³

In the molecular structure of **4a**, established by an X-ray diffraction analysis (Figure 5), each of the silicon atoms exhibits a distorted-tetrahedral geometry and the vertex of the Si(I) atom is occupied by a lone pair of electrons. The Si–Si distance of 2.413(2) Å is about 0.07 Å longer than the sum of the silicon covalent radii (2.34 Å)⁴⁴ (Si–Si single bond) and is similar to that of $\text{NHC} \rightarrow \text{Si}(\text{Cl})\text{Si}(\text{Cl}) \leftarrow \text{NHC}$ (2.393 Å).⁴² The Si–Si single bond in **4a** can be cleaved by Br_2 to form the bromo NHSi **22**.⁴⁵ Due to the structural similarities to **3**, its intriguing reactivity with regard to small-molecule activation is included in this account.

The very recent successful synthesis of the bis-phosphane Si(I)–Si(I) complex **4b** is quite similar to the route applied for the formation of **4a**. The reduction of the corresponding trichlorosilane derivative using 3 molar equiv of elemental lithium in THF at room temperature afforded **4b** as red crystals in 13% yield (Scheme 6).²⁵ In the ^{29}Si NMR spectrum, the latter exhibits a doublet of doublets at δ –18.5 ppm ($^1J_{\text{SiP}} = 192.1$ Hz, $^2J_{\text{SiP}} = 60.1$ Hz), indicating the

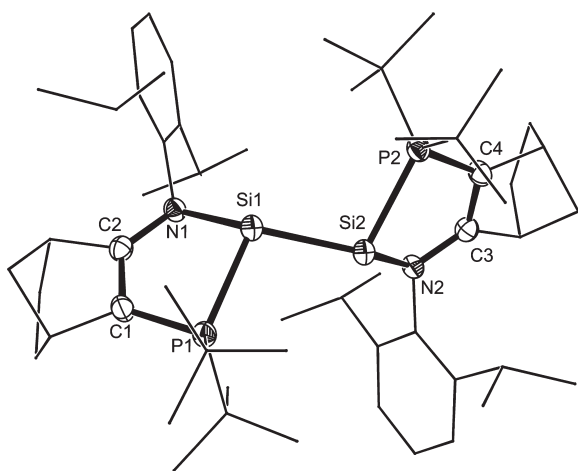
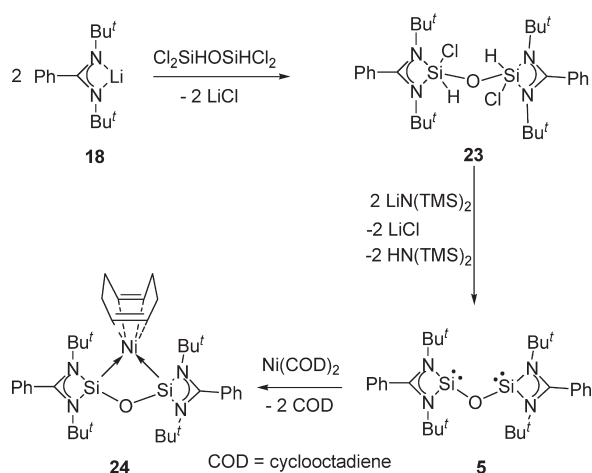


Figure 6. Molecular structure of **4b** with thermal ellipsoids drawn at the 50% probability level.

Scheme 7. Synthesis and Coordination of Bis-Silylene Oxide **5**



presence of two phosphorus atoms in the molecule. The ^{31}P NMR spectrum displays only one singlet at δ 34.7 ppm.

The molecular structure of **4b** established by X-ray crystallography reveals a cis-bent geometry for the N–Si–Si–N skeleton with a torsion angle of 4.98° (Figure 6). Each silicon atom interacts with a phosphorus center on both sides of the Si_2N_2 plane, forming two five-membered rings. Most interestingly, the Si–Si distance of 2.331(1) Å is significantly shorter than those observed for **4a** (2.413(2) Å)⁴¹ and $\text{NHC}\rightarrow\text{Si}(\text{Cl})\text{Si}(\text{Cl})\leftarrow\text{NHC}$ (2.393 Å),⁴² suggesting some multiple-bond (disilyne-like) character for the Si–Si bonding interaction in **4b**, which should give rise to a different reactivity pattern in comparison with **4a**.

2.5. Synthesis and Coordination of Bis-Silylene Oxide **5.** Dehydrochlorination of respective chlorosilane using strong bases, e.g. NHCs or amides, has been reported to generate several stable NHSi's and appears to be a powerful method for generating low-valent silicon species.⁴⁶ Very recently the first isolable bis(silylene) oxide **5** was also successfully synthesized using this strategy (Scheme 7).²⁶ The 2-fold dehydrochlorination of bis-amidinate-substituted chlorodisiloxane **23**, resulting from the reaction of 1,1,3,3-tetrachlorodisiloxane, $\text{Cl}_2\text{SiH}-\text{O}-\text{SiHCl}_2$, with 2 molar equiv of

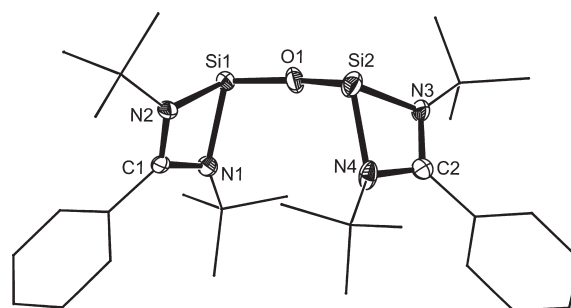


Figure 7. Molecular structure of **5** with thermal ellipsoids drawn at the 50% probability level.

lithium amidinate **18**, led to the formation of the desired product **5** in 76% yield.

The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **5** shows a singlet at δ –16.1 ppm, which is upfield with respect to the chlorosilylene **3** (14.6 ppm) but comparable to those of the related silylene alkoxides **21b** (–5.2 ppm) and **21c** (–13.5 ppm), respectively. Compound **5** features a molecular structure similar to that of bis-NHSi **4a**, however, with an oxygen atom as a bridge between the two Si(II) centers (Figure 7). The two Si–O bonds (1.641(2) and 1.652(2) Å) as well as the Si–O–Si angle of $159.9(2)^\circ$ fall in the geometric parameter ranges for disiloxanes and those of the mixed-valent Si(II)–O–Si(IV) disiloxane **2** (see section 3). With two divalent silicon centers, **5** is capable of reacting with $[\text{Ni}(\text{COD})_2]$ (COD = cycloocta-1,3-diene) to furnish the unique bis(silylene) oxide nickel(0) complex **24** (Scheme 7).²⁶

3. REACTION OF SILYLENE **1** WITH H_2O , $\text{H}_2\text{O}-\text{B}(\text{C}_6\text{F}_5)_3$, AND H_2S

Akin to other known stable silylenes, **1** is very sensitive toward moisture. Simple addition of liquid water to a solution of **1** led merely to complete hydrolysis and formation of the “free” β -diketiminate ligand **6**. However, as mentioned in section 2.2, slow diffusion of water vapor into a hexane solution of **1** at 4°C afforded **2** as brown-red crystals in 52% yield (Scheme 8).²⁰ The reaction of **1** with water has some similarities to the case for other known silylenes, which activate both O–H bonds of the water molecule to give a disiloxane.^{8,9,11,47} Notably, **2** was the only detectable product (^1H NMR) even when an excess of **1** was applied. The mechanism is still unknown. However, the main difference of **1** compared to other NHSi's with respect to water addition is that the first step of reaction of H_2O with **1** proceeds heterolytically in a 1,4-fashion to form the intermediate **25**, due to the presence of both the electrophilic (oxophilic) Si(II) site and Brønsted basic exocyclic methylene group. The formation of **2** suggests that proton migration from a terminal methyl group to the silicon center in **25** to form the transient **26** seems to be much faster than the proton transfer from the OH group to the divalent silicon atom, preventing the formation of silaforamide **27**.

It is worth mentioning that a second proton migration in **2** from one of the other exocyclic methyl groups to the Si(II) center is also possible. In fact, the disiloxane species **28** has been obtained as yellow crystals in the presence of trace amounts of a proton source (e.g., silica) as catalyst (Scheme 8).⁴⁸ In contrast, the isomerization can be easily avoided by using a small amount of triethylamine. Unlike its precursor **2**, compound **28** is symmetric and possesses only one stereoisomer, as indicated by NMR spectroscopy and X-ray diffraction analysis. In comparison to the structural parameters of

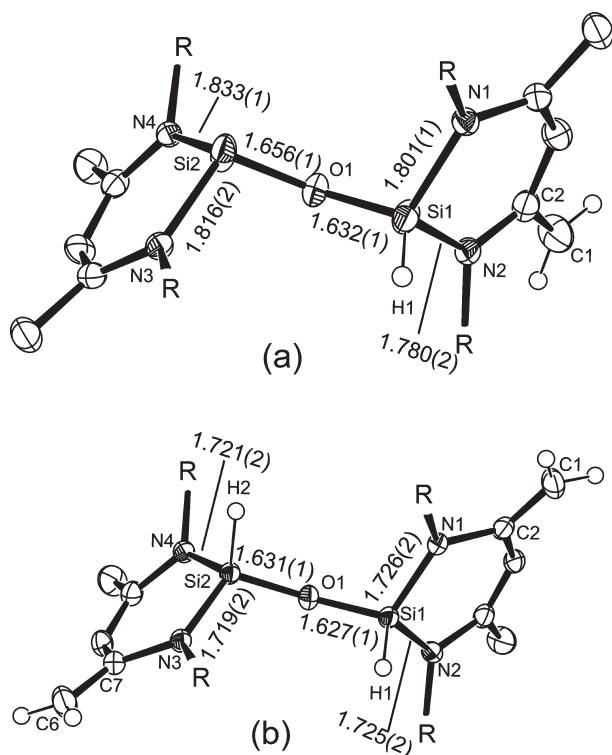
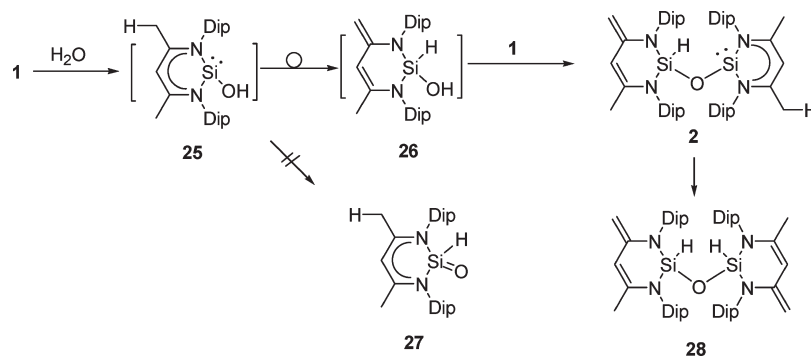
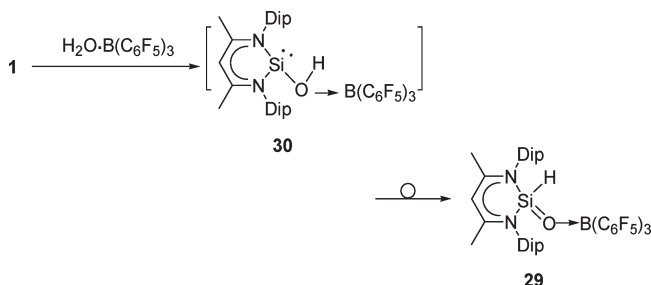
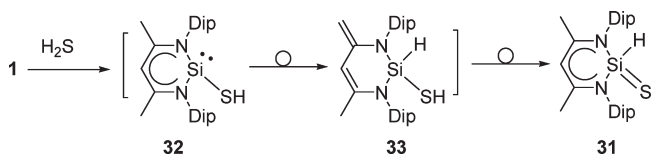
Scheme 8. Reaction of **1** with H₂O

Figure 8. Comparison of selected parameters of the molecular structure of **2** (a) with those of **28** (b). Thermal ellipsoids are drawn at the 50% probability level. The H atoms, except those at C1 and C6, are omitted for clarity. R = 2,6-Prⁱ₂C₆H₃.

2, the Si–N distances of **28** are significantly shorter and the Si–O distances are practically identical (Figure 8).

Interestingly, the reaction of **1** with the much stronger Brønsted acid H₂O–B(C₆F₅)₃ adduct led solely to the donor–acceptor stabilized silaformamide–borane adduct **29**. A mechanism via formation of intermediate **30** as a 1,4-adduct has been proposed (Scheme 9).²⁰ Subsequent OH proton migration to the silicon center in **30** furnished the final product **29**, which proved stable enough to be isolated and completely characterized. In the molecular structure of **29**, the silicon atom of the silaformyl group (Si(H)=O) is tetrahedrally coordinated due to an intramolecularly dative N→Si bond and features a remarkably short silicon–oxygen interatomic distance of 1.552(2) Å, about 7% shorter than those observed in silyl ethers (Si–O–C) and common disiloxanes (Si–O–Si).⁴⁹ In line

Scheme 9. Reaction of **1** with H₂O–B(C₆F₅)₃Scheme 10. Reaction of **1** with H₂S

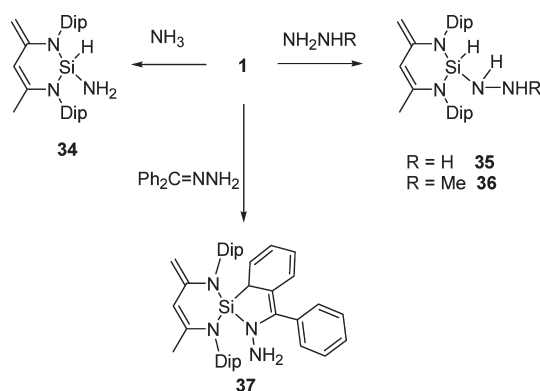
with that, a relatively high Si–O stretching frequency of 1165 cm^{−1} was observed, indicating some Si=O character. In fact, a population analysis for **29** in terms of natural atomic orbitals revealed a significant population for the two antibonding Si–N bonds ($\sigma^*\pi$ -acceptor orbitals mainly located at silicon) and a decreased population for the two oxygen lone pairs (n_π -donor orbitals), which indicated a substantial π -bonding interaction between these orbitals.²⁰

NHSi **1** also reacts readily with H₂S to give the donor-stabilized silathioformamide **31** in excellent yield (Scheme 10).⁵⁰ Analogous to the reaction of **1** with water, the two possible intermediates **32** and **33** were suggested. The facile formation of **31**, which is in sharp contrast to the water activation product **2**, could be attributed to the higher Brønsted acidity of H₂S compared to that of H₂O. Compound **31** represents the first isolable donor-stabilized silathioformamide. As expected, the Si=S distance of 1.9854(9) Å in **31** is significantly shorter than Si–S single bonds (ca. 2.14 Å).⁵¹

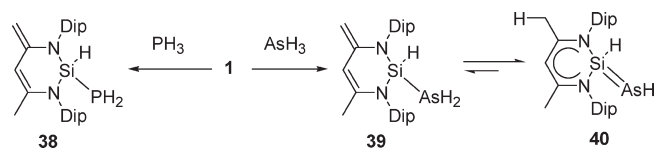
4. ACTIVATION OF N–H BOND IN AMMONIA AND HYDRAZINES WITH **1**

Recently, activation of the N–H bonds of ammonia has attracted considerable attention.⁵² Interestingly, and akin to

Scheme 11. Activation of Ammonia, Hydrazines, and a Hydrazone with **1**



Scheme 12. Activation of PH_3 and AsH_3 with **1**



the case for NHCs,^{21b} **1** is capable of metal-free activation of ammonia. When dry ammonia was allowed to pass through a solution of **1**, a reaction rapidly took place and the 1,1 N–H bond insertion product **34** was isolated in high yield (90%) (Scheme 11).⁵³ This reactivity is unprecedented for other stable silylenes. Additionally, **1** activates N–H bonds of hydrazine and methylhydrazine to give the 1,1-insertion products **35** and **36**, respectively.⁵⁴ However, **1** reacts with diphenyl hydrazone in toluene differently to afford the dearomatized siloxy-indolin-1-amine **37** in almost quantitative yield. In this reaction, no insertion of the Si(II) center into the N–H bond of the NH_2 group has been observed.

5. ACTIVATION OF PH_3 AND AsH_3

In contrast to the reaction with NH_3 , the activation PH_3 with **1** proceeds much more slowly, leading to the expected 1,1-addition product, silylphosphane **38** (Scheme 12).⁵⁵ Accordingly, a 20-fold excess of PH_3 was used to complete the conversion. The reaction of **1** with AsH_3 takes place again very quickly, owing to the greater Brønsted acidity. Unexpectedly, arsilene **40** was isolated as dark blue crystals from the resulting solution in 48% yield (Scheme 12).

Although the expected 1,1-addition product **39**, a tautomer of **40**, has not been isolated from the reaction mixture, it does exist in solution, as indicated by ^1H NMR spectroscopy. In fact, dissolution of pure **40** in benzene leads to equilibrium with a minor amount of **39**. Compound **40** represents a unique donor-stabilized arsilene with a $\text{HSi}=\text{AsH}$ subunit. Its molecular structure established by X-ray diffraction analysis revealed a rather short Si–As distance (2.2178(1) Å), which lies between those of single (2.36 Å) and double bonds (2.16 Å)⁵⁶ and suggests a significant $\text{Si}=\text{As}$ character. Accordingly, MO analysis of the corresponding model system of **40**, in which the 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3$ substituents were replaced with phenyl groups, exhibited a reduced Wiberg bond index of 1.465 compared

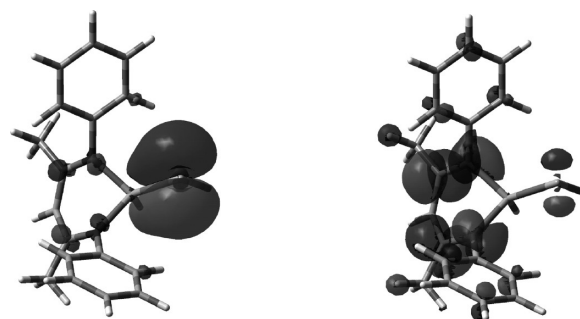
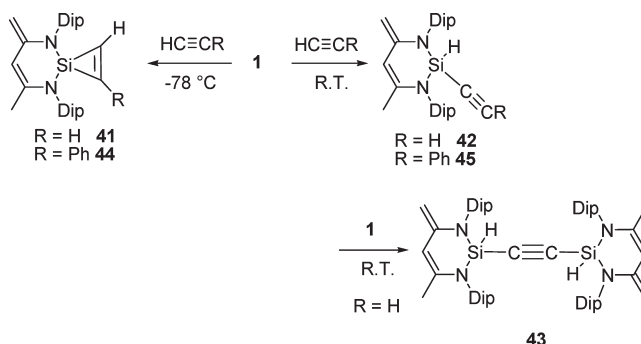


Figure 9. HOMO (left) and LUMO (right) of a model compound for **40**.

Scheme 13. Activation of Acetylene and Terminal Alkynes with **1**

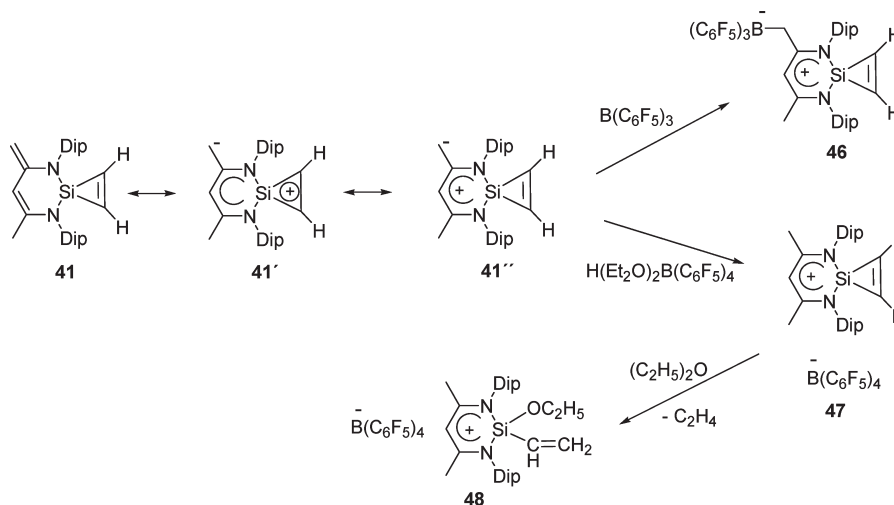


with that of the reference system $(\text{H}_2\text{N})_2\text{Si}=\text{AsH}$ (1.643). The weakening of the $\text{Si}=\text{As}$ bond character in **40** with respect to those $\text{Si}=\text{As}$ systems with a three-coordinate silicon atom is presumably due to the dative $\text{N} \rightarrow \text{Si}$ interaction. The deep blue color of **40** is caused by the HOMO ($\text{Si}=\text{As} \pi$) \rightarrow LUMO ($\text{Si}=\text{As} \pi^*$) transition, consistent with results of DFT calculations (Figure 9).

The different reactivities of **1** toward NH_3 , PH_3 , and AsH_3 have been investigated in more detail by DFT calculations on the respective model systems, in which the bulky 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3$ substituents were replaced by phenyl groups.⁵⁵ The relative energy of the model compound for **40** is 5.7 kcal mol^{-1} lower than that of the 1,1-addition product **39**, which is in good agreement with the experimental results described above. In the case of NH_3 , the model system of the 1,1-addition product **34** is at least 14.7 kcal mol^{-1} more stable than its tautomeric iminosilane. This also accounts well for the exclusive formation of **34** in the reaction of **1** with ammonia.⁵³ The calculated relative energy of a model of the phosphasilene analogue of **40** is slightly lower (3.0 kcal mol^{-1}) than that of the 1,1-addition product **38** resulting from the reaction of **1** with PH_3 ; nevertheless, only **38** was obtained and no experimental evidence has been found for the formation of the corresponding phosphasilene in the reaction, even at low temperature.⁵⁵

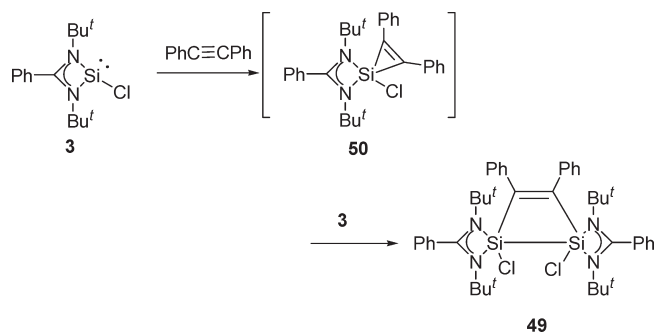
6. ACTIVATION OF TERMINAL ALKYNES: C–H ACTIVATION VS [2 + 1] CYCLOADDITION

Astonishingly, the activation of parent acetylene by **1** is temperature dependent: at relatively low temperature (-78°C) **1** slowly undergoes [2 + 1] cycloaddition with acetylene to give the silacycloprip-3-ene **41** as the only product (Scheme 13).⁵⁷

Scheme 14. Reaction of **41** with $\text{B}(\text{C}_6\text{F}_5)_3$ and $[\text{H}(\text{Et}_2\text{O})_2]\text{B}(\text{C}_6\text{F}_5)_4$ 

At room temperature, however, C–H activation and scission occurs very quickly, leading exclusively to terminal alkynylsilane **42**. Interestingly, after an induction period of a few hours at low temperature ($-78\text{ }^\circ\text{C}$), the same starting materials surprisingly undergo only $[2 + 1]$ cycloaddition at room temperature to furnish **41** in several hours. More practically, the latter cycloaddition can also be conducted by using a small amount of **41** prior to the introduction of acetylene into solutions of **1**. While the reaction of **1** with diphenylacetylene only led to the formation of the corresponding silacycloprop-3-ene $[2 + 1]$ cycloadduct, **1** and phenylacetylene undergo reactions similar to that of **1** and the parent acetylene, affording either **44** or **45** depending on the reaction conditions. Moreover, a second C–H activation of the acetylene molecule can also occur by the treatment of **42** with **1** equiv of **1** in hexane at room temperature (Scheme 13). Thus, 1,2-disilylacetylene **43** could also be isolated in the form of colorless crystals in high yield. It is further noteworthy that neither facile silylene C–H bond insertion for parent acetylene (or related terminal alkyne derivatives) nor formation of isolable silacycloprop-3-ene starting from other isolable silylenes has been reported previously.⁵⁸

Consistent with results from DFT calculations, **41** and **42** cannot interconvert into each other for kinetic reasons.⁵⁷ Although the mechanism of the peculiar formation of the $[2 + 1]$ cycloaddition product **41** at low temperature is still unknown, an autocatalytic process based on the ylide-like resonance structures **41'** and **41''** (Scheme 14) has been proposed.⁵⁷ In line with that, theoretical calculations predicted a relatively large proton affinity of the exocyclic methylene group in **41** ($1111.6\text{ kJ mol}^{-1}$) and the dipole moment of **41** is relatively large (experimental 3.1 D vs calculated 2.3 D). Thus, **41** could serve as auxiliary bases capable of mediating the $[2 + 1]$ cycloaddition of **1** with terminal alkynes vs C–H activation (silylene insertion). The ylide resonance structure **41'** enabled the reaction of **41** with $\text{B}(\text{C}_6\text{F}_5)_3$ to form the first isolable, zwitterionic silacyclopropenylium–boranide adduct **46** in high yield.⁵⁹ Moreover, protonation of **41** with the convenient Brønsted acid $[\text{H}(\text{OEt}_2)_2]^+\text{B}(\text{C}_6\text{F}_5)_4^-$ led to quantitative formation of the corresponding silacyclopropenylium salt **47**. In the presence of diethyl ether, the highly electrophilic Si atom

Scheme 15. Reaction of **3** with Diphenylacetylene

in **47** slowly mediates a striking C–O bond cleavage to release ethylene and **48**.

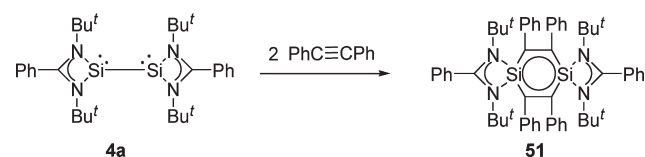
The reactivity of chlorosilylene **3** toward diphenylacetylene has also been examined.³⁹ The unexpected resultant disilacyclobutene **49** was isolated from the reaction mixture in 42% yield (Scheme 15). It was postulated that, after an initial cyclopropanation reaction to form **50**, an insertion of a second equivalent of **3** into one of the Si–C bonds occurred to yield **49**.

The addition of 2 equiv of diphenylacetylene to **4a** has recently been reported as well.⁶⁰ Both diphenylacetylene equivalents add across the Si–Si bond in **4a**, with concomitant Si–Si bond scission, to give the 1,4-disilabenzene derivative **51** with an unprecedented electronic situation at silicon (Scheme 16). The disilabenzene moiety is almost planar in the solid state, despite the tetrahedral silicon centers, and theoretical calculations support the presence of some aromatic character ($\text{NICS}(1) = -3.6$).

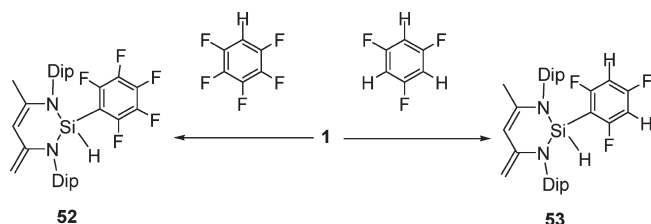
7. SILICON-MEDIATED ACTIVATION OF C–H AND C–F BONDS IN FLUOROBENZENES

NHSi **1** reacts with pentafluorobenzene ($\text{C}_6\text{F}_5\text{H}$) at room temperature with chemoselective formation of the corresponding arylsilicon(IV) hydride **52** in high yield (Scheme 17).⁶¹ The latter reaction occurs via oxidative addition of the aromatic C–H bond onto the Si(II) center instead of C–F bond activation,

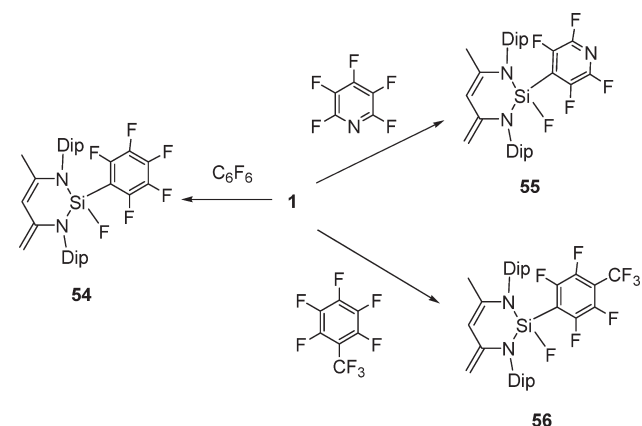
Scheme 16. Reaction of 4a with Diphenylacetylene



Scheme 17. C–H Activation of Pentafluorobenzene and 1,3,5-Trifluorobenzene with 1



Scheme 18. C–F Activation of Hexafluorobenzene, Pentafluoropyridine, and Octafluorotoluene with 1



presumably due to a smaller C–H bond energy compared to that of the C–F bonds. Likewise, **1** can also activate one of the C–H bonds in 1,3,5-trifluorobenzene (1,3,5- $\text{C}_6\text{F}_3\text{H}_3$) at ambient temperature, which leads to the formation of **53** in good yield.

Nevertheless, **1** is also capable of activating aromatic C–F bonds in hexafluorobenzene (C_6F_6), octafluorotoluene ($\text{C}_6\text{F}_5\text{CF}_3$), and pentafluoropyridine ($\text{C}_5\text{F}_5\text{N}$) without any additional catalyst, yielding the corresponding arylsilyl fluorides **54**–**56** through oxidative addition of a C–F bond to the Si(II) center (Scheme 18).⁶¹ In the case of the reactions with octafluorotoluene and pentafluoropyridine, regioselective C–F bond activation occurred as well, leading to the formation of **55** and **56**, respectively.

Similarly, the chlorosilylene **3** can also activate aromatic C–F bonds in hexafluorobenzene (C_6F_6), octafluorotoluene ($\text{C}_6\text{F}_5\text{CF}_3$), and pentafluoropyridine ($\text{C}_5\text{F}_5\text{N}$) to give the corresponding five-coordinate silicon(IV) fluorides **57**–**59** (Scheme 19).⁶¹ Regioselective C–F bond cleavage takes place as well in the reaction with octafluorotoluene and pentafluoropyridine, affording **58** and **59** as the main products, respectively. In contrast to the reactivity of NHSi

1 toward pentafluorobenzene, the reaction of **3** with this fluoroarene led to chemoselective as well as regioselective C–F bond activation, producing the five-coordinate **60** in high yield.

8. ACTIVATION OF HALOALKANES AND HALOSILANES WITH 1

NHSi **1** is capable of activating haloalkanes. However, this reactivity is significantly different from that of other NHSi's. The insertion of the other NHSi's into a C–X bond ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) of haloalkanes, on the basis of a free-radical mechanism, is strongly dependent on the nature of the haloalkane molecules.⁶² In most of the cases, the latter reactions end up with the formation of disilanes of the type $\text{LSi}(\text{X})\text{--Si}(\text{R})\text{L}$ (L = supporting ligand, X = halide) and the doubly 1,1-inserted compounds $(\text{LSiX})_2\text{CR}_2$, respectively. In contrast, the insertion of **1** into C–X bonds of haloalkanes yielded exclusively the 1,1-insertion products $\text{LSi}(\text{R})\text{X}$ and in some cases also small amounts of dihalosilanes LSiX_2 .⁶³

As shown in Scheme 20, the reaction of **1** with the mono-haloalkane MeI furnished solely the 1,1-insertion product **61**. In addition, **1** inserts readily into the aliphatic C–Br bond of PhCH_2Br , yielding the corresponding 1,1-insertion product **62**. The reaction of **1** with CH_2Cl_2 afforded the 1,1-insertion product **63** in almost quantitative yield, while the analogous reaction with CH_2ClI led exclusively to the iodo(chloromethyl)silane **64**, irrespective of the relative molar ratio of the starting materials. Moreover, the reaction of **1** with CH_2Br_2 afforded the 1,1-insertion product **65** along with dibromosilane **8a** in 58 and 42% yields, respectively. Even treatment of **1** with perhalogenated hydrocarbons afforded the respective 1,1-insertion products. This has been shown by the reaction of **1** with CHCl_3 and MeCCl_3 to give chloro(dichloroalkyl)silanes **66** and **67**, respectively, along with a small amount of dihalosilane **8b**.

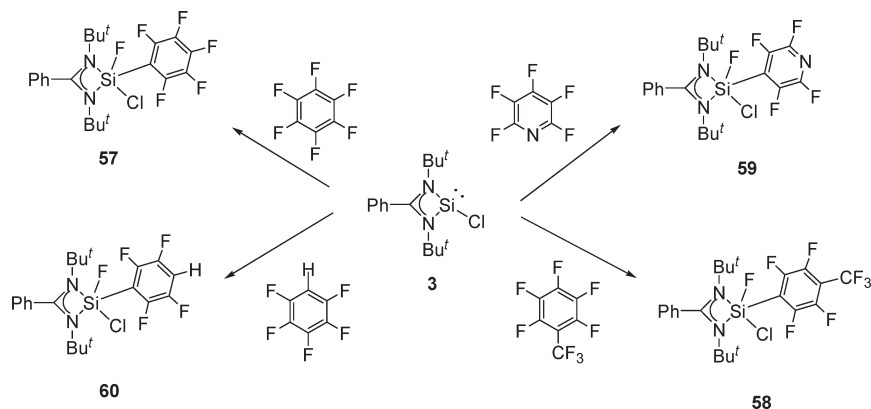
Likewise, the reaction of **1** with the trichlorosilanes HSiCl_3 and MeSiCl_3 leads to the corresponding main products **68** and **69**, respectively (Scheme 21). In both cases, the minor product **70** has been identified by NMR spectroscopy and mass spectrometry. Sterically more congested chlorosilanes such as Ph_2SiCl_2 and PhSiCl_3 are resistant toward **1**.

9. ACTIVATION OF UNSATURATED ORGANIC FUNCTIONAL GROUPS

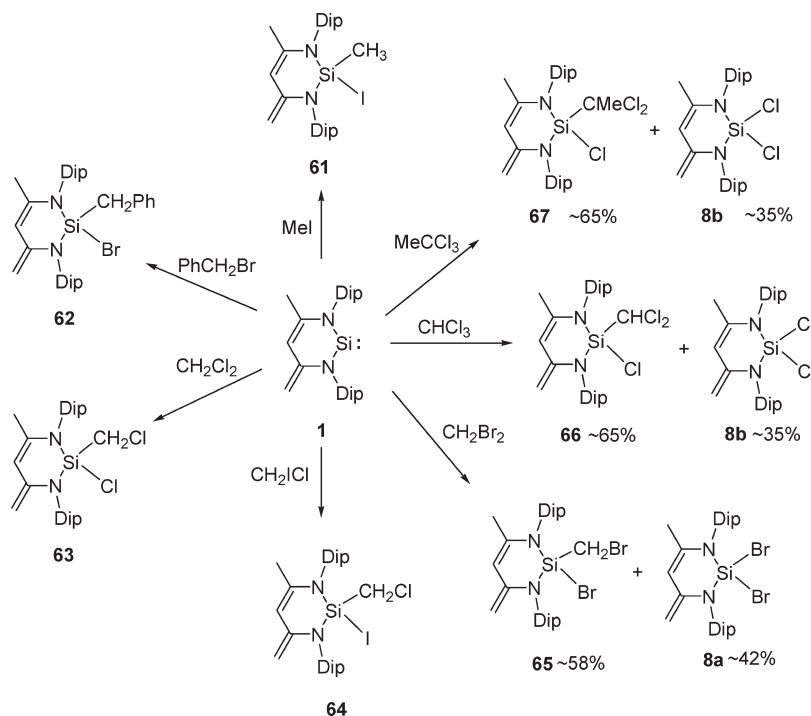
Akin to the behavior of the divalent silicon atom in **1** toward C–C triple bonds in alkynes (see section 6), it was expected that the carbene-like electron deficiency of the Si(II) atom enables a variety of cycloaddition reactions with other unsaturated organic functional groups to yield silaheterocycles. In fact, **1** reacts with 2,3-dimethylbuta-1,3-diene in hexane even at low temperature, yielding the expected $[4 + 1]$ cycloadduct **71** (Scheme 22).⁶⁴ Similarly, the reaction of **1** with benzylideneacetone yielded the $[4 + 1]$ cycloadduct **72**.⁶⁵

Remarkably, the reaction of **1** with benzophenone at -78°C led for the first time to the isolation of the unusual $[4 + 1]$ cycloaddition product **73**, containing a methylenecyclohexadiene moiety which resulted from concomitant dearomatization of a phenyl group (Scheme 22). The tendency of **73** to undergo rearomatization of the cross-conjugated methylene-cyclohexadiene π system facilitated its slow tautomerization to **74** even at room temperature. The latter has also been isolated and structurally characterized. Related intermediates of **73** with a nonaromatic siloxindane ring system have been

Scheme 19. C–F Bond Activation of Fluorobenzenes with 3



Scheme 20. Activation of Haloalkanes with 1



previously proposed but could not be detected for similar reactions of transient silylenes⁶⁶ and a stable silylene⁶⁷ with benzophenone, respectively.

Unexpectedly, the reaction of **1** with the heteroatom π -conjugated acetone azine initially afforded the unusual [3 + 1] cycloadduct **75**,⁶⁴ the first zwitterionic 1-sila-2,3-diazacyclobutane, which subsequently underwent isomerization in solution to give the 1-sila-2,3-diazacyclobutane **76**. The latter isomerized further in solution at room temperature by ring expansion and release of strain energy of the four-membered SiCN₂ ring in **76**, yielding 1-sila-4,5-diazacyclohex-3-ene **77**. In contrast, the isoelectronic 1,1,4,4-tetramethylbuta-1,3-diene did not react with **1**, even at 50 °C. As mentioned above, employing the less bulky 2,3-dimethylbuta-1,3-diene furnished the expected [4 + 1] cycloadduct **71**.

The reaction of **1** with diphenyldiazomethane led to the isolation of the first diiminylsilane, LSi(N=CPh₂)₂ (**78**) (Scheme 23).⁶⁸ Moreover, treatment of **1** with trimethylsilyl azide afforded solely the corresponding silatetrazoline **79**, instead of formation of the corresponding iminosilane. Such iminosilanes have been formed in the case of silylene **Ia**⁶⁹ and **Ic**.⁷⁰ Conversion of **1** with cyclohexyl isocyanide yielded not only silacyanide **80** but also the remarkable azasilacyclobutane **81**;⁶⁸ the latter resulting via a cascade of coupling reactions of three isocyanide molecules and 2-fold C–H activation and intramolecular hydrogen atom transfer. The simple Lewis adduct **82** was not detected in the resulting mixture, although a similar adduct has been isolated by Kira and co-workers with silylene **V**.⁷¹

Very interesting results from the reaction of **3** with benzophenone have also been reported.⁷² In this case, the [1 + 2]

cycloaddition occurred and the first siloxirane **83**, with a three-membered SiOC ring and a pentacoordinate silicon center, could be isolated (Scheme 24). Additionally, the reactivity of **3** toward 1,2-diphenyl-1,2-ethanedione (benzil) was examined. The reaction with equimolar amounts of benzil led to the formation of the [1 + 4] cycloaddition product **84** in good yield.

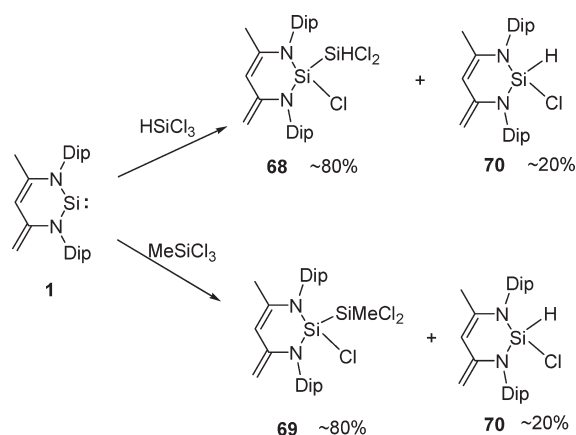
The reactivity of the bis-NHSi **4a** toward benzophenone and benzil has also been described.⁷³ In the case of the reaction of **4a** with 2 equiv of benzophenone, the unexpected dioxasilatane **85** with a four-membered Si₂O₂ ring (Scheme 25) has been formed and isolated. The formation of **85** involved Si–Si bond rupture and deoxygenation of the C=O bond of benzophenone with **4a**. In contrast, the reaction with 2 molar equiv of benzil led to the formation of the 2-fold [1 + 4] cycloaddition product **86**.⁷⁴ In

this case, the Si–Si bond was retained and its bond length of 2.36 Å is even slightly shorter than that in **4a** (2.41 Å).

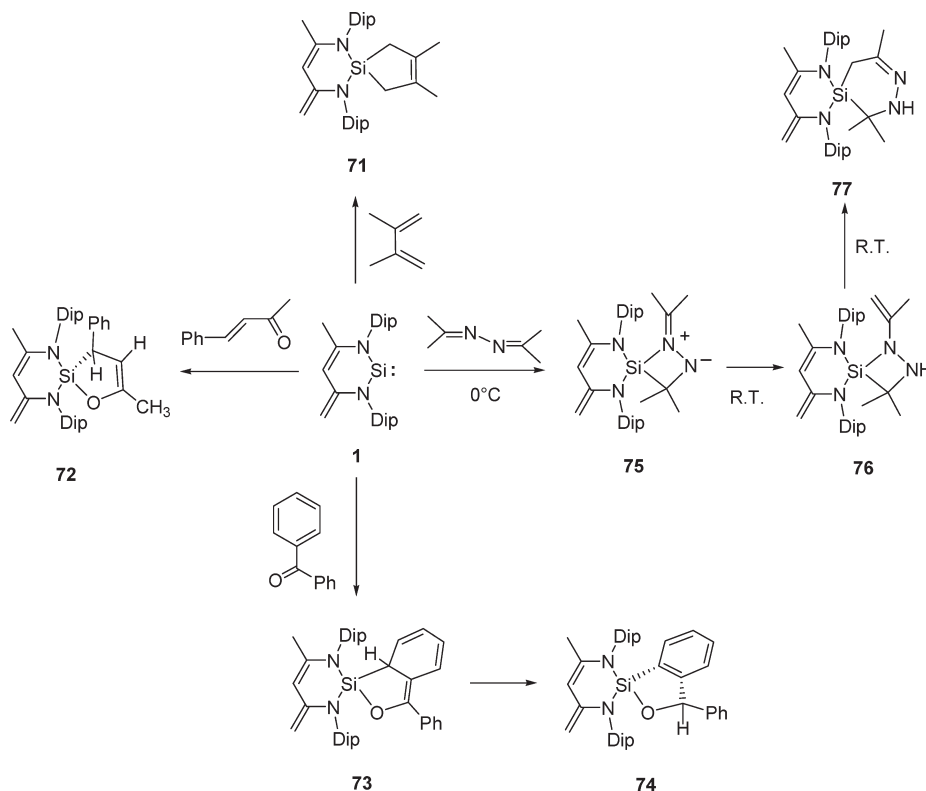
10. ACTIVATION OF WHITE PHOSPHORUS (P₄)

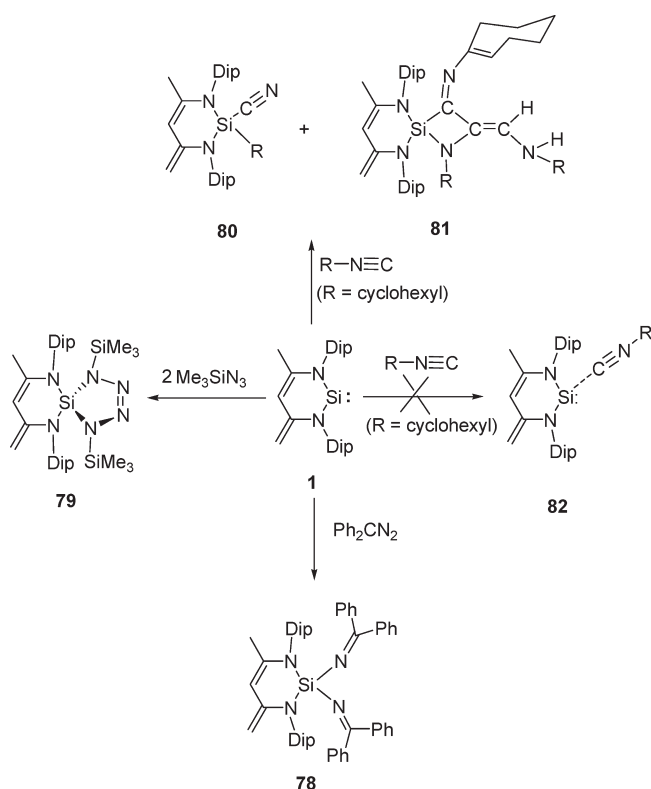
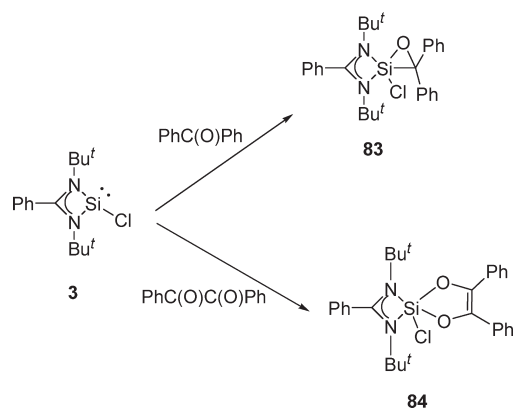
Apart from the facile, metal-free activation of white phosphorus employing NHCs and even diamino cyclopropenylidenes,^{75,76} no similar reaction for stable silylenes, except for the brief mention that perhaps **1a** catalyzes the transformation of white phosphorus to the more stable red phosphorus allotrope,^{47b} was reported until recently. In 2007 we reported that **1** reacts directly with P₄ at room temperature in toluene, leading to the formation of two activation products which differ from those reported for NHCs (Scheme 26).⁷⁷ One of the products is the 1:1 adduct **87**, resulting from Si(II) atom insertion of 1 molar equiv of **1** into a P–P bond of the P₄ tetrahedron. A second equivalent of **1** could also be inserted into another P–P bond of **87** to give the isolable 2:1 adduct **88** with a Si₂P₄ skeleton. Both products have been isolated and fully characterized. Interestingly, **87** reacts with [Ni^I(β-diketiminate)]₂·(toluene) complexes to give the doubly P–P activated mixed P₄ complex **89**.⁷⁸ Recently, theoretical studies on the activation of P₄ by an NHSi of type **1** have been reported.^{79,80} Accordingly, an electrophilic attack at P₄ was suggested by Schoeller as an initial step of this process.⁷⁹ This is in sharp contrast to the behavior of NHC's, which prefers a nucleophilic attack at P₄, affording a cyclotriphosphene species.⁷⁶ Remarkably, the electrophilic approach of the NHSi is catalyzed by addition of a second P₄ molecule, forming a trigonal bipyramid at the Si(II) center as a transition state which subsequently decomposes to **87** and P₄. It is worth mentioning that similar P₄ activation with Al(β-diketiminate) has been reported by Roesky et al.; however, only the doubly activated analogue of **88** was observed and isolated.⁸¹

Scheme 21. Si–X Bond Activation of Halosilanes with **1**



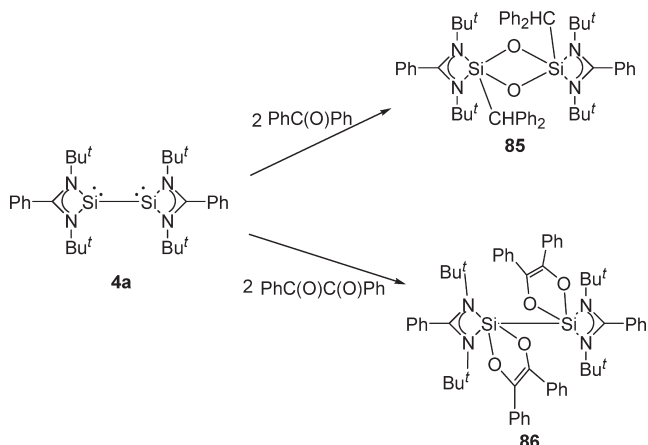
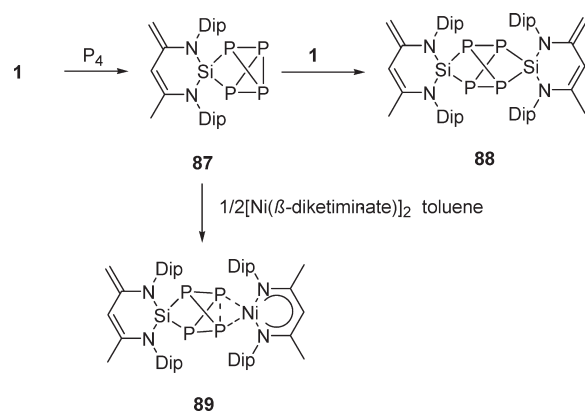
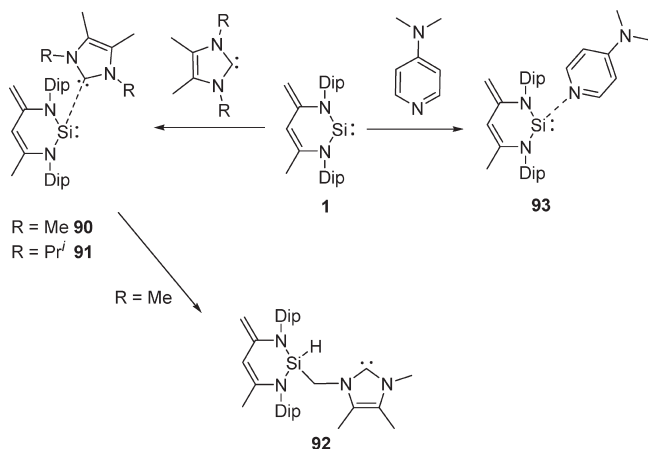
Scheme 22. Activation of Selected Unsaturated Organic Functional Groups with **1**



Scheme 23. Reaction of **1** with Selected Unsaturated Organic Functional GroupsScheme 24. Reaction of **3** with Benzophenone and Benzil

11. ACTIVATION OF N_2O AND CO_2

Although direct activation of N_2O or CO_2 with **1** failed, by introducing a strong donor, e.g. through donor coordination of NHCs or 4-dimethylaminopyridine (DMAP) to the Si(II) center of **1**, the activation became successful due to the “Umpolung” of the Si(II) site. Thus, the NHC→Si(II) adducts **90** and **91** were accessible in high yields from the reaction of **1** with the 1,3,4,5-tetramethylimidazol-2-ylidene or 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (Scheme 27).^{82,83} Remarkably, adduct **90** is not stable at room temperature and slowly undergoes rearrangement to furnish the new silyl-substituted NHC **92** through

Scheme 25. Activation of Benzophenone and Benzil with **4a**Scheme 26. Activation of White Phosphorus with **1**Scheme 27. Umpolung of the Si(II) atom in **1** through Donor Coordination of NHC and DMAP Ligands

insertion of the Si(II) center into one C–H bond of an *N*-methyl group of **90**.⁸³ The NHC **92** has been isolated and also structurally characterized. In contrast, the NHC adduct **91** is

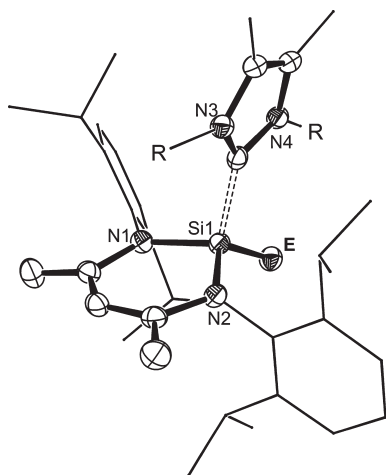
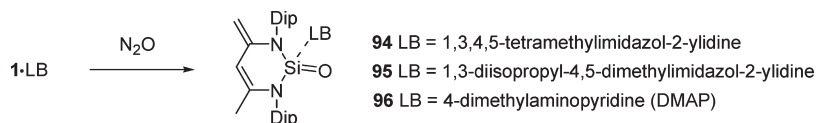
Scheme 28. Oxygenation of **90**, **91**, and **93** with N_2O 

Figure 10. Molecular structures of **94** ($\text{R} = \text{Me}$, $\text{E} = \text{O}$), **95** ($\text{R} = \text{Pr}^i$, $\text{E} = \text{O}$), **112a** ($\text{R} = \text{Pr}^i$, $\text{E} = \text{S}$), **112b** ($\text{R} = \text{Me}$, $\text{E} = \text{S}$), **113a** ($\text{R} = \text{Pr}^i$, $\text{E} = \text{Se}$), **113b** ($\text{R} = \text{Me}$, $\text{E} = \text{Se}$), **114a** ($\text{R} = \text{Pr}^i$, $\text{E} = \text{Te}$), and **114b** ($\text{R} = \text{Me}$, $\text{E} = \text{Te}$) with thermal ellipsoids drawn at the 50% probability level.

stable even at elevated temperature. Likewise, the less basic DMAP ligand also coordinates readily to the $\text{Si}(\text{II})$ center of **1** to give the stable adduct **93**.⁸⁴

Exposure of toluene solutions of complex **90**, **91**, and **93** at room temperature to N_2O immediately furnished the corresponding desired $\text{Si}=\text{O}$ adducts **94–96** (Scheme 28), respectively.^{82,84,85} The resultant species **94–96** all feature a terminal oxygen atom with remarkably short $\text{Si}-\text{O}$ distances, ranging from 1.527(2) to 1.5412(2) Å (Figure 10). Because of coordination of the Lewis base (NHC or DMAP) to the silicon atoms, the hypothetical sila-urea $\text{N}_2\text{Si}=\text{O}$ moieties in the latter complexes lose their planarity and thus the silicon atoms adopt a distorted-tetrahedral geometry.

It should be mentioned that the isolation of silanones ($\text{R}_2\text{Si}=\text{O}$) that are stable at room temperature (“Kipping’s dream”)⁸⁶ could not be achieved as yet. The absence of isolable silanones is probably due to the pronounced polarity of the silicon–oxygen π bond and hence the extraordinary high tendency of silanones to undergo oligomerization.⁸⁷ However, taking advantage of the donor–acceptor stabilization concept, the donor-stabilized $\text{Si}=\text{O}$ double bond species **94–96** are sufficiently stable for isolation at ambient temperature.

Despite of the $\text{LB} \rightarrow \text{Si}=\text{O}$ stabilization, these adducts are suitable silanone analogues for the elucidation of the $\text{Si}=\text{O}$ reactivity toward both electrophilic and nucleophilic reagents. Owing to the intrinsically strong polarity (ylide character) of the $\text{Si}=\text{O}$ subunit, the DMAP-stabilized silanone **96** reacts readily with trimethylaluminum and dimethylzinc to give the corresponding Lewis adducts.⁸⁸ In contrast, the reaction of **96** with zinc acetate furnished $\text{Si}=\text{O}$ addition products. More interestingly, the silanone complex **96** can activate ammonia under mild conditions after replacement of the DMAP ligand to give the

intriguing sila-heminaminal **97** (Scheme 29).⁸⁴ Related hemiaminals of carbon analogues are generally elusive and can only be detected with special environments.⁸⁹ In accordance with DFT calculations, **97** undergoes tautomerization to yield the unprecedented silanoic amide derivative **98**. Compounds **97** and **98** are observed in equilibrium both in solution and in the solid state with an $\text{SiOH} \cdots \text{O}=\text{Si}$ interaction. In the solid state, the $\text{Si}-\text{O}$ distances of 1.545(2) and 1.546(2) Å in **98** revealed the presence of a $\text{Si}=\text{O}$ bond, while the $\text{Si}-\text{O}$ bond length of 1.607(2) Å in **97** is close to a normal $\text{Si}-\text{O}$ bond.

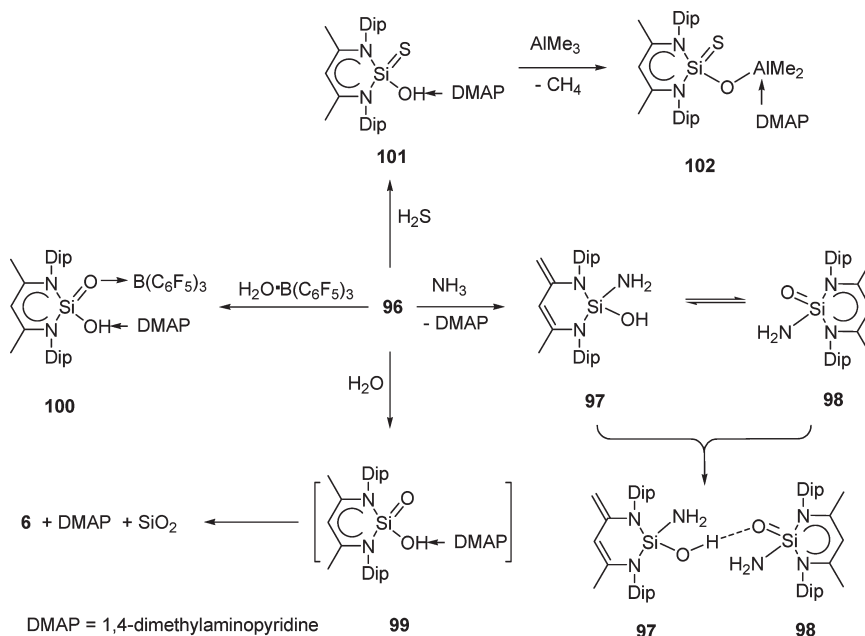
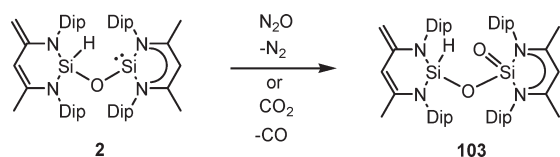
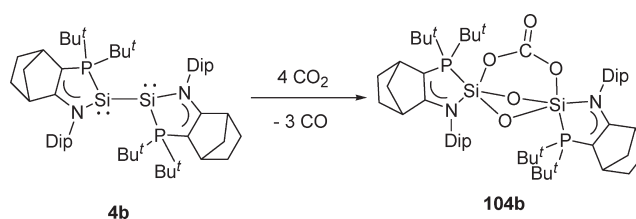
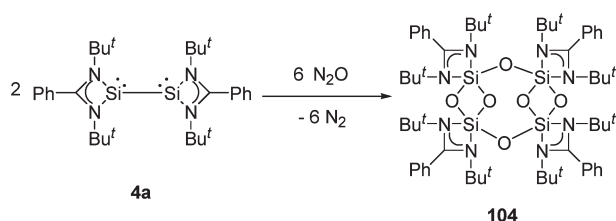
The reaction with water by exposing a solution of **96** in THF to H_2O vapor at room temperature led merely to the parent β -diketiminato ligand **6** and “free” DMAP along with the precipitation of SiO_2 (Scheme 29).⁹⁰ Attempts to synthesize the silacarboxylic (“silanoic”) acid–base complex **99** by addition of water to **96** at low temperature ($<0^\circ\text{C}$) was hitherto unsuccessful. However, the conversion of **96** with $\text{H}_2\text{O}-\text{B}(\text{C}_6\text{F}_5)_3$ furnished the first isolable $\text{LSi}(\text{=O})\text{OH}$ complex in the form of $[\text{LSi}(\text{OH} \cdots \text{DMAP})(\text{=O} \rightarrow \text{B}(\text{C}_6\text{F}_5)_3)]$ (**100**) in almost quantitative yield.

In contrast to the reaction with water, the addition of H_2S to **96** led to the desired product **101**, which could be isolated as yellow crystals in excellent yield (Scheme 29). The $\text{Si}-\text{S}$ bond length of 1.993(1) Å observed in the molecular structure of **101** is close to that value for **31** (1.985(1) Å) and indicates a significant $\text{Si}=\text{S}$ bond character. Notably, **101** does not undergo a 1,3-proton shift to give the possible $\text{LSi}(\text{=O})\text{SH} \cdots \text{DMAP}$ isomer, presumably due to the weaker $p_\pi-p_\pi$ bond and the higher bond polarity of $\text{Si}=\text{O}$ compared with the $\text{Si}=\text{S}$ subunit.³¹ Featuring the unique $\text{Si}(\text{=S})\text{OH}$ subunit, **101** represents the first silathiocarboxylic acid–base adduct. The latter compound reacted easily with organometallic bases to form metal silathiocarboxylates. Accordingly, treatment of **101** with 1 molar equiv of AlMe_3 in toluene at ambient temperature furnished the aluminum silathiocarboxylate $\text{LSi}(\text{=S})(\text{OAlMe}_2(\text{DMAP}))$ (**102**) with the DMAP coordinated at the Al atom.

The activation of CO_2 has been unsuccessful with the donor-supported NHSis **90**, **91**, and **93**. Interestingly, both CO_2 and N_2O can be activated by using the intramolecular donor-stabilized siloxy silylene **2**, leading to the same isolable silanoic silyl ester **103** along with the liberation of dinitrogen and carbon monoxide, respectively (Scheme 30).²¹ The $\text{Si}-\text{O}$ distance of 1.579(3) Å in **103** is slightly longer than those observed in the aforementioned NHC’s and DMAP-stabilized $\text{Si}=\text{O}$ species **94–96**.^{82,84,85} The latter formation of **103** on application of CO_2 as monooxygen source represents the first $\text{Si}(\text{II})$ -mediated CO_2 activation with an NHSi.

Very recently, the reaction of bis-NHSi **4a** with N_2O has been reported to give the siloxy compounds **104** (Scheme 31).⁷³ This species was fully characterized, and a mechanism for its formation was suggested by the authors. It contains two four-membered disiloxane rings bridged by two oxygen atoms and represents a new class of silicon–oxygen compounds.

Scheme 29. Reactivity of DMAP-Stabilized Silanone 96

Scheme 30. Activation of N_2O and CO_2 with 2Scheme 32. Activation of CO_2 with 4bScheme 31. Activation of N_2O with 4a

Another fascinating CO_2 activation by a low-valent silicon species was reported very recently: Bacereido et al. described the oxygenation of bis(silylene) **4b** with CO_2 to give the striking carboxylato bis-silicate **104b** in high yield (Scheme 32).²⁵ The formation of **104b** requires consumption of 4 molar equiv of CO_2 .

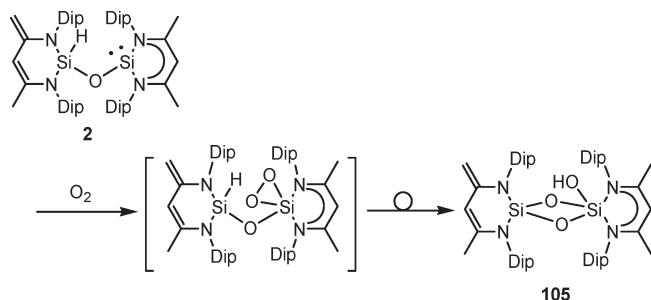
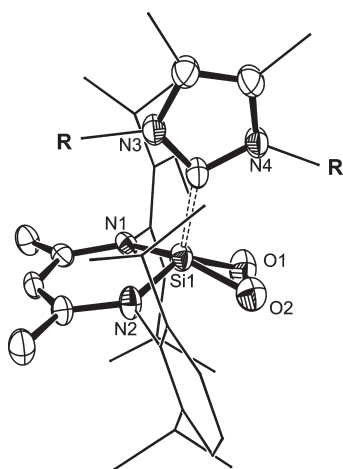
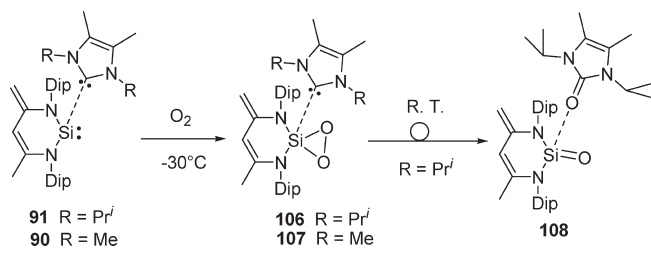
12. ACTIVATION OF O_2

Due to the presence of Si(II) centers, all stable silylenes are sensitive toward dioxygen. The reactivity of stable silylenes toward O_2 was studied extensively, with the hope of isolating a monomeric Si=O -containing species. Nevertheless, only $[2 + 2]$ dimers with a four-membered Si_2O_2 ring could be obtained as

isolable products.⁸ In line with that, **1** reacts also readily with dry dioxygen, affording only an unidentified mixture of products. However, more nucleophilic Si(II) atoms as present in intramolecular donor-stabilized siloxy silylene **2** are capable of reacting readily with dioxygen to furnish the isolable cyclodisiloxane **105** in high yield (Scheme 33).²¹ Most likely, the reaction proceeds via a side-on $\text{Si} \cdots \text{O}_2$ complex which subsequently rearranged to yield **105** as the final product.

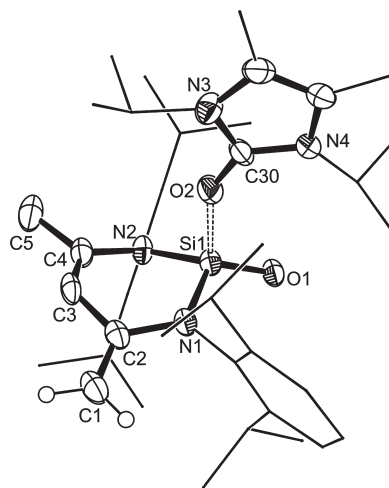
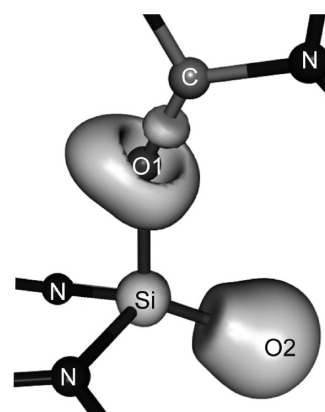
Very interestingly, the $\text{NHC} \rightarrow \text{NHSi}$ complexes **90** and **91** can undergo controlled activation of dioxygen, first to give the isolable dioxasilirane adducts **106** and **107**, which have been isolated at low temperature (-30°C) in crystalline form and fully characterized (Scheme 34).⁹¹ The O_2 ligand in both **106** and **107** is “side-on” coordinated to the tetravalent silicon atom and lies almost within the $\text{C}_3\text{N}_2\text{Si}$ ring plane (Figure 11). Unexpectedly, the five-coordinate Si atom adopts a square-pyramidal coordination for steric reasons. The compounds **106** and **107** represent the first isolable silicon peroxide species with a “side-on” O_2 ligand. The $\text{O}-\text{O}$ distances of 1.547(3) Å in **107** and 1.510(3) Å in **106**, respectively, are slightly longer than that in dimesityldioxirane (1.50 Å)⁹² and those observed for related “side-on” metal peroxo complexes (1.4–1.5 Å).⁹³

When it was warmed to room temperature, the dioxasilirane adduct **106** rearranged in toluene by transferring one oxygen

Scheme 33. Activation of O₂ with **2**Scheme 34. Activation of O₂ with **90** and **91**Figure 11. Molecular structure of **106** (R = Prⁱ) and **107** (R = Me) with thermal ellipsoids drawn at the 50% probability level.

atom to the NHC-carbene center to give the ketone (cyclourea)-stabilized silanone (cyclic sila-urea) **108** (Scheme 34). Complex **108** was isolated as colorless crystals, which features the shortest Si–O distance (1.532(1) Å) in a Si=O-containing molecular compound ever structurally characterized (Figure 12).

The relatively long Si1–O2 distance to the cyclourea moiety (1.727(2) Å) and the short O–C distance (1.294(3) Å) suggested a dative interaction between the cyclourea and the cyclic sila-urea moieties. This is well supported by DFT calculations of the model compound, in which the 2,6-Prⁱ₂C₆H₃ groups at nitrogen in the C₃N₂ skeleton were replaced by methyl substituents and the organic groups in the cyclourea moiety by hydrogen atoms. The natural resonance theory (NRT) bond orders and the Wiberg bond indices as well as plots of the electron localization function (ELF) (Figure 13) are in accordance with the coordinative nature of the

Figure 12. Molecular structure of **108** with thermal ellipsoids drawn at 50% probability level.Figure 13. Electron localization function (ELF) representation (ELF surface = 0.80 isosurface) of the Si–O₂ versus C–O₁ and C–O₁→Si bonding of a model compound of **108** (B3LYP/TZVPP//RI-BP86/TZVP).

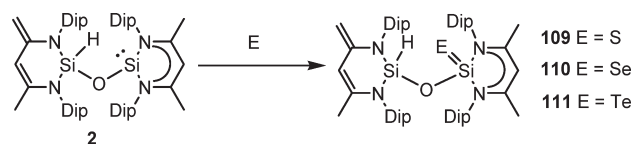
C=O→Si interaction. Additionally, the large ionicity of the Si=O bond in the model compound was clearly shown from ELF plots.

13. ACTIVATION OF ELEMENTAL SULFUR, SELENIUM, AND TELLURIUM

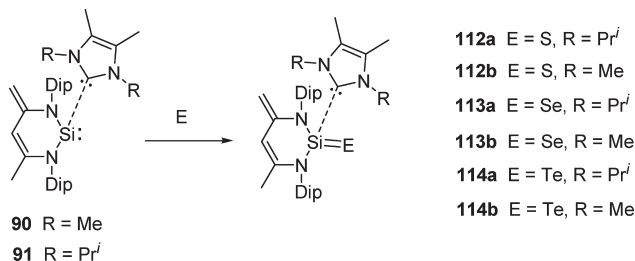
Both intra- and intermolecular donor-supported NHSi's (**2**, **90**, and **91**) can activate elemental sulfur, selenium, and tellurium to give the corresponding donor-stabilized heavier silanone or silanoic silyl ester congeners.^{85,94} For instance, siloxyl silylene **2** is capable of activating heavier elemental chalcogens in toluene at room temperature, affording the N-donor-stabilized silanechalcogenones **109–111** in high yields (Scheme 35).

Likewise, the reaction of NHC→NHSi adducts **90** and **91** with the respective elemental chalcogens in toluene at room temperature led to the formation of the expected NHC-supported silanechalcogenones **112a,b–114a,b** (Scheme 36). The latter have been isolated and fully characterized, including X-ray diffraction (Figure 12). In addition, the nature of the Si=S double bonds in **103** and the Si=O double bonds in **109** have been even thoroughly investigated by solid-state NMR and high-level calculations.³¹ In spite of the fact that the Si=E bond is

Scheme 35. Activation of Elemental Chalcogens with 2



Scheme 36. Activation of Elemental Chalcogens by 90 and 91



donor-stabilized, careful analysis of the analytical data indicated that there is significant Si–E double-bond character in these species.

14. CONCLUSION AND OUTLOOK

It is hoped that this review has demonstrated the striking and powerful potential of the ylide-like NHSi **1**, the first halogen-substituted NHSi **3**, and the bis-NHSi's **2**, **4a,b**, and **5**, which are suitable for facile, low-valent, silicon-based small-molecule activation. Their reactivity pattern differs from those of other known stable silylenes and opens new doorways to silicon-based building blocks and functional groups. For instance, the exocyclic methylene group in **1**, which may behave as an additional nucleophilic group, cooperates with the two genuine Si(II) reactive sites (a lone pair and an empty 3p orbital) and makes this species more capable of activating X–Y bonds in small molecules under gentle reaction conditions. The activation that directly led to the formation of isolable, doubly bonded silicon species, such as Si=S- and Si=As-containing compounds, represents long sought after achievements in contemporary silicon chemistry. Owing to the presence of an unsaturated silicon atom, **1** exhibits carbene-like reactivity toward small unsaturated organics to furnish a variety of new organosilanes. Moreover, it undergoes unique consecutive P–P bond activation of white phosphorus (P₄), affording organosilicon–phosphorus compounds by a metal-free route. Remarkably, the nucleophilicity of the Si(II) centers can be significantly increased and tuned by introducing strong donors (e.g., NHCs, DMAP, and cyclic imine) datively bonded to silicon (“Umpolung”). The latter chemical trick broadened the suitability and performance of NHSi's for activation of small molecules such as N₂O, CO₂, and O₂ and gives rise to novel isolable silicon species which otherwise are extremely difficult to obtain (e.g., silanone, silanoic acid and dioxasilirane derivatives).

Replacing precious metal or even utilizing nonmetals for small-molecule activation and catalysis is an emergent field in synthetic chemistry which is in its infancy (or in the case of “organocatalysis” is in a renaissance). It is hoped that this account will stimulate more extensive studies with respect to silicon (and

other nonmetal)-based small-molecule activation for the synthesis of value-added products. This includes the exploration and utilization of transition-metal complexes with the aforementioned multifunctional NHSi ligands for facile bond activation.⁹⁵ It seems particularly interesting to gain access to catalytically active NHSi's and their metal complexes in the near future.

■ ASSOCIATED CONTENT

S Supporting Information. A CIF file giving crystallographic data for **28**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

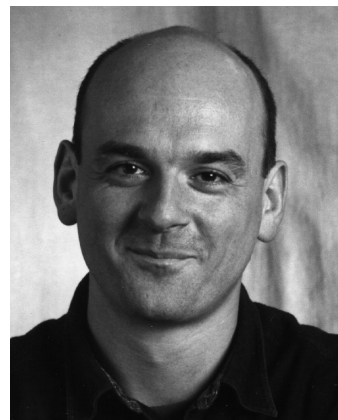
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Notes

[†]Activation of small molecules refers here to the activation of species that are difficult to activate such as CO₂, N₂O, NH₃, etc. It also includes reactions with O₂, P₄, H₂O, and H₂S, respectively.

■ BIOGRAPHIES



Matthias Driess was born in Eisenach, Germany. He completed his Diploma degree in Chemistry at the University of Heidelberg in 1985 and, in addition, studied Philosophy at the University of Heidelberg. His Ph.D. degree was gained in the field of boron-phosphorus chemistry from the University of Heidelberg, under the supervision of Professor Walter Siebert in 1988. He then worked from 1988 to 1989 as a postdoctoral fellow at the University of Wisconsin at Madison with Professor Robert West. He returned to the University of Heidelberg and finished his Habilitation in 1993. In 1996 he accepted a position as a full professor of Inorganic Chemistry at the University of Bochum (Germany) before moving to a full professorship at the Institute of Chemistry (Metalorganic Chemistry and Inorganic Materials) of the Technische Universität Berlin (2004). Since 2007 he has served as a spokesperson of the Cluster of Excellence “Unifying Concepts in Catalysis” (UniCat) in the Berlin-Potsdam area. He has been the recipient of several awards, including the Alfred-Stock-Memorial-Award of the German Chemical Society in 2010. His current research interests include the coordination chemistry of main-group elements and transition

metals in unusual coordination and oxidation states and the synthesis of functional inorganic materials, e.g. heterometal oxide nanoparticles, employing molecular architecture. In these and related areas he has published more than 200 papers.



Shenglai Yao was born in Guangxi, People's Republic of China. He studied chemistry and completed his B.Sc. degree at the Hua-Zhong Normal University in 1988. From 1988 to 1997 he worked as a Research Officer at the Hua-Zhong Normal University. His M.Sc. was gained from the same University, under the supervision of Professor Guanghan Lu in 2000. He then moved to Germany, where he began his doctoral research under the supervision of Prof. Dr. Karl W. Klinkhammer and received his Ph.D. degree in 2005 at the Johannes Gutenberg University of Mainz. Afterwards he joined the research group of Prof. Dr. Matthias Driess at the Technische Universität Berlin and continues to work in the group as senior researcher. Dr. Yao has a strong research interest in organometallic chemistry of the heavier main-group and transition-metal elements. He has contributed to the development of a series of highly reactive metal-free and transition-metal systems for small-molecule activation.



Yun Xiong was born in the People's Republic of China and received her M.Sc. degree from Yunnan University, Kunming, People's Republic of China. Her Ph.D. degree was gained from the Johannes Gutenberg University of Mainz in Germany under the supervision of Prof. Dr. Karl W. Klinkhammer. Before she came to Germany, she worked at the Wuhan University of Science and Technology and the Hua-Zhong Normal University, Wuhan, People's Republic of China, for several years as a lecturer of chemistry and as an associate professor of chemistry, respectively. In 2006 she joined the research group of Prof. Dr. Matthias

Driess at the Technische Universität Berlin as a research fellow. Her research is currently focused on main-group chemistry, with particular emphasis on the design and synthesis of new isolable silylene and silanone species.

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■ REFERENCES

- (1) Ottosson, H.; Steel, P. G. *Chem. Eur. J.* **2006**, *12*, 1576–1585.
- (2) (a) Gaspar, P. P.; Xiao, M.; Pae, D. H.; Berger, D. J.; Haile, T.; Chen, T.; Lei, D.; Winchester, W. R.; Jiang, J. P. *J. Organomet. Chem.* **2002**, *646*, 68–79. (b) Lee, V. Y.; Sekiguchi, A. Heavy Analogs of Carbenes: Silylenes, Germylenes, Stannylenes and Plumbylens. In *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb*; Wiley: London, 2010; Chapter 4, pp 139–197.
- (3) (a) Sekiguchi, A.; Tanaka, T.; Ichinohe, M.; Akiyama, K.; Teo-Kubota, S. *J. Am. Chem. Soc.* **2003**, *125*, 4962–4963. (b) Holthause, M. C.; Koch, W.; Apeloig, Y. *J. Am. Chem. Soc.* **1999**, *121*, 2623–2624.
- (4) Weidenbruch, M. *Coord. Chem. Rev.* **1994**, *130*, 275–300.
- (5) Denk, D.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691–2692.
- (6) Kong, L.; Zhang, J.; Song, H.; Cui, C. *Dalton Trans.* **2009**, 5444–5446.
- (7) West, R.; Denk, M. *Pure Appl. Chem.* **1996**, *68*, 785–788.
- (8) Li, W.; Hill, N. J.; Tomasik, A. C.; Bikzhanova, G.; West, R. *Organometallics* **2006**, *25*, 3802–3805.
- (9) Tomasik, A. C.; Mitra, A.; West, R. *Organometallics* **2009**, *28*, 378–381.
- (10) Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Mueller, T.; Bukalov, S.; West, R. *J. Am. Chem. Soc.* **1999**, *121*, 9479–9480.
- (11) Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Blaaser, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1931–1932.
- (12) Heinicke, J.; Oprea, A.; Kindermann, M. K.; Karpati, T.; Nyulaszi, L.; Veszpremi, T. *Chem. Eur. J.* **1998**, *4*, 541–545.
- (13) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1383–1386.
- (14) Review on silylenes: (a) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354–396. (b) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479–3511. (c) Kira, M.; Iwamoto, T.; Ishida, S. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 258–275. (d) Takeda, N.; Tokitoh, N. *Synlett* **2007**, 16, 2483–2491. (e) Hill, N. J.; West, R. *J. Organomet. Chem.* **2004**, *689*, 4165–4183. (f) Kira, M. *J. Organomet. Chem.* **2004**, *689*, 4475–4488. (g) Okazaki, M.; Tobita, H.; Ogino, H. *Dalton Trans.* **2003**, 493–506. (h) Gehrhus, B.; Lappert, M. F. *J. Organomet. Chem.* **2001**, *617*, 209–223. (i) Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704–714.
- (15) Lee, G.-H.; West, R.; Müller, T. *J. Am. Chem. Soc.* **2003**, *125*, 8114–8115.
- (16) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, *121*, 9722–9723.
- (17) (a) Kira, M.; Iwamoto, T.; Ishida, S. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 258–275. (b) Kira, M. *J. Organomet. Chem.* **2004**, *689*, 4475–4488.
- (18) Kühler, T.; Jutzi, P. *Adv. Organomet. Chem.* **2003**, *49*, 1–34.
- (19) Driess, M.; Yao, S.; Brym, M.; van Wüllen, C.; Lentz, D. *J. Am. Chem. Soc.* **2006**, *128*, 9628–9629.
- (20) Yao, S.; Brym, M.; van Wüllen, C.; Driess, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4159–4162.

- (21) Yao, S.; Xiong, Y.; Brym, M.; Driess, M. *J. Am. Chem. Soc.* **2007**, *129*, 7268–7269.
- (22) Selected reviews: (a) Stephan, D. W. *Chem. Commun.* **2010**, 46, 8526–8533. (b) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, *2*, 389–399. (c) Power, P. P. *Nature* **2010**, *463*, 171–177.
- (23) So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 3948–3950.
- (24) Sen, S. S.; Jana, A.; Roesky, H. W.; Schulzke, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 8536–8538.
- (25) Gau, D.; Rodriguez, R.; Kato, T.; Saffon-Merceron; C  zar, A. Cosso, F. P.; Baceiredo, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 1092–1096.
- (26) Wang, W.; Inoue, S.; Yao, S.; Driess, M. *J. Am. Chem. Soc.* **2010**, *132*, 15890–15892.
- (27) Feldmann, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514–1516.
- (28) Ding, Y.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 1190–1194.
- (29) Xiong, Y.; Yao, S.; Driess, M. *Dalton Trans.* **2009**, 421–423.
- (30) Xiong, Y.; Yao, S.; Driess, M. *Chem. Asian J.* **2009**, *4*, 1323–1328.
- (31) Epping, J. D.; Yao, S.; Karni, M.; Apeloig, Y.; Driess, M. *J. Am. Chem. Soc.* **2010**, *132*, 5443–5455.
- (32) West, R.; Buffy, J. J.; Haaf, M.; M  ller, T.; Gehrhus, B.; Lappert, M. F.; Apeloig, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1639–1640.
- (33) Driess, M.; Yao, S.; Brym, M.; van Wuelen, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 6730–6733.
- (34) Wang, R. -H.; Su, M. -D. *J. Phys. Chem. A* **2008**, *112*, 7689–7698.
- (35) Jutzi, P.; Mix, A.; Rummel, B.; Schoeller, W. W.; Neumann, B.; St  mmler, H. -G. *Science* **2004**, *305*, 849–851.
- (36) (a) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781–4788. Review: (b) King, R. B.; Schleyer, P. v. R. Theory and Concepts in Main-Group Cluster Chemistry. In *Molecular Clusters of the Main Group Elements*; Driess, M.; N  th, H., Eds.; Wiley-VCH: Weinheim, Germany, 2004; pp 1–33.
- (37) Driess, M.; Yao, S.; Brym, M.; van W  llen, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 4349–4352.
- (38) (a) So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 3948–3950. (b) Weidenbruch, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 4241–4242.
- (39) Sen, S. S.; Roesky, H. W.; Stern, D.; Henn, J.; Stalke, D. *J. Am. Chem. Soc.* **2010**, *132*, 1123–1126.
- (40) So, C.-W.; Roesky, H. W.; Gurubasavaraj, P. M.; Oswald, R. O.; Gamer, M. T.; Jones, P. G.; Blaurock, S. *J. Am. Chem. Soc.* **2007**, *129*, 12049–12054.
- (41) Sen, S. S.; Jana, A.; Roesky, H. W.; Schulzke, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 8536–8538.
- (42) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *Science* **2008**, *321*, 1069–1071.
- (43) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. *Science* **2004**, *305*, 1755–1757.
- (44) Corey, J. Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Vol. 1, Chapter 1.
- (45) Yeong, H.-X.; Lau, K.-C.; Xi, H.-W.; Lim, K. H.; So, C.-W. *Inorg. Chem.* **2010**, *49*, 371–373.
- (46) (a) Cui, H.; Shao, Y.; Li, X.; Kong, L.; Cui, C. *Organometallics* **2009**, *28*, 5191–5195. (b) Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 5683–5686.
- (47) (a) Haaf, M.; Schmedake, T. A.; Paradise, B. J.; West, R. *Can. J. Chem.* **2000**, *78*, 1526–1533. (b) Haaf, M.; Schmiedl, A.; Schmedake, T. A.; Powell, D. R.; Millevolte, A. J.; Denk, M.; West, R. *J. Am. Chem. Soc.* **1998**, *120*, 12714–12719.
- (48) Analytical data for 28: mp 243   C dec; ¹H NMR (400.13 MHz, C₆D₆, 298 K)    0.41 (d, ³J_{HH} = 7 Hz, 6 H, CMe₂), 0.64 (d, ³J_{HH} = 7 Hz, 6 H, CMe₂), 1.19 (d, ³J_{HH} = 7 Hz, 6 H, CMe₂), 1.20 (d, ³J_{HH} = 7 Hz, 6 H, CMe₂), 1.23 (d, ³J_{HH} = 7 Hz, 6 H, CMe₂), 1.32 (d, ³J_{HH} = 7 Hz, 6 H, CMe₂), 1.38 (d, ³J_{HH} = 7 Hz, 6 H, CMe₂), 1.46 (s, 6 H, NCM₂), 1.69 (d, ³J_{HH} = 7 Hz, 6 H, CMe₂), 3.05 (sept, ³J_{HH} = 7 Hz, 2 H, CHMe₂), 3.10 (s, 2 H, NCCCH₂), 3.18 (sept, ³J_{HH} = 7 Hz, 2 H, CHMe₂), 3.55 (sept, ³J_{HH} = 7 Hz, 2 H, CHMe₂), 3.82 (s, 2 H, NCCCH₂), 4.03 (sept, ³J_{HH} = 7 Hz, 2 H, CHMe₂), 4.56 (s, 2 H, SiH, ²⁹Si satellites: ¹J_{HSi} = 285 Hz), 5.29 (s, 2 H, γ-CH), 6.91–7.26 ppm (m, br, 12 H, arom H); ¹³C{¹H} NMR (100.61 MHz, C₆D₆, 298 K)    14.3–31.9 (NCMe, ¹Pr); 88.7 (NCCCH₂), 107.5 (γ-C); 124.8–149.7 ppm (2,6-¹Pr₂C₆H₃, NC); ²⁹Si NMR (79.49 MHz, C₆D₆, 298 K):    -55.0 ppm (d, ¹J_{HSi} = 285 Hz, SiH); EI-MS m/z (%) 907 (13, [M]⁺), 892 (100, [M - Me]⁺), 864 (44, [M - ¹Pr]⁺). Anal. Calcd for C₅₈H₈₂N₄Si₂O: C, 76.7; H, 9.1; N, 6.2. Found: C, 75.9; H, 9.2; N, 5.7.
- (49) Sheldrick, W. S. Structural Chemistry of Organic Silicon Compounds; In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989, Vol. 1, Chapter 3, p 227.
- (50) Meltzer, A.; Inoue, S.; Praesang, C.; Driess, M. *J. Am. Chem. Soc.* **2010**, *132*, 3038–3046.
- (51) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, Part 1, pp 228–233.
- (52) See for examples: (a) Zhao, J.; Goldman, A. S.; Hartwig, J. F. *Science* **2005**, *307*, 1080–1082. (b) Frey, G. D.; Lavallo, V.; Donnadi  u, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439–441. (c) Peng, Y.; Ellis, B. D.; Wang, X.; Power, P. P. *J. Am. Chem. Soc.* **2008**, *130*, 12268–12269. (d) Chase, P. A.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 7433–7437.
- (53) Jana, A.; Schulzke, C.; Roesky, H. W. *J. Am. Chem. Soc.* **2009**, *131*, 4600–4601.
- (54) Jana, A.; Roesky, H. W.; Schulzke, C.; Samuel, P. P. *Organometallics* **2009**, *28*, 6574–6577.
- (55) Pr  sang, C.; Stoelzel, M.; Inoue, S.; Melter, A.; Driess, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 10002–10005.
- (56) (a) Driess, M.; Rell, S.; Pritzkow, H. *J. Chem. Soc., Chem. Commun.* **1995**, 253–254. (b) Driess, M. *Coord. Chem. Rev.* **1995**, *145*, 1–25.
- (57) Yao, S.; van Wuelen, C.; Sun, X.-Y.; Driess, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3250–3253.
- (58) (a) Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 3715–3716. (b) Tho Nguyen, M.; Sengupta, D.; Vanquickenborne, L. G. *Chem. Phys. Lett.* **1995**, *240*, 513–520. (c) Becerra, R.; Frey, H. M.; Mason, B. P.; Walsh, R. J. *Chem. Soc., Chem. Commun.* **1993**, 1050–1052. (d) Haas, C. H.; Ring, M. A. *Inorg. Chem.* **1975**, *14*, 2253–2256.
- (59) Yao, S.; Xiong, Y.; van Wuelen, C.; Driess, M. *Organometallics* **2009**, *28*, 1610–1612.
- (60) Sen, S. S.; Roesky, H. W.; Kathrin, Meindl; Stern, D.; Henn, J.; St  ckl, A. C.; Stalke, D. *Chem. Commun.* **2010**, 46, 5873–5875.
- (61) Jana, A.; Samuel, P. P.; Tav  ar, G.; Roesky, H. W.; Schulzke, C. *J. Am. Chem. Soc.* **2010**, *132*, 10164–10170.
- (62) (a) Moser, D. F.; Naka, A.; Guzei, L. A.; M  ller, T.; West, R. *J. Am. Chem. Soc.* **2005**, *127*, 14730–14738. (b) Delawar, M.; Gehrhus, B.; Hitchcock, P. B. *Dalton Trans.* **2005**, 2945–2953. (c) Gehrhus, B.; Hitchcock, P. B.; Jansen, H. J. *Organomet. Chem.* **2006**, *691*, 811–816. (d) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Chem. Lett.* **2001**, 1102–1103.
- (63) Xiong, Y.; Yao, S.; Driess, M. *Organometallics* **2009**, *28*, 1927–1933.
- (64) Xiong, Y.; Yao, S.; Driess, M. *Organometallics* **2010**, *29*, 987–990.
- (65) Xiong, Y.; Yao, S.; Driess, M. *Chem. Eur. J.* **2009**, *15*, 5545–5551.
- (66) (a) Ando, W.; Ikeno, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **1977**, *99*, 6447–6449. (b) Ando, W.; Ikeno, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **1978**, *100*, 3613–3615. (c) Ando, W.; Hamada, Y.; Sekiguchi, A.; Ueno, K. *Tetrahedron Lett.* **1982**, *23*, 5323–5326. (d) Belzner, J.; Ihmels, H.; Pauletto, L. J. *Org. Chem.* **1996**, *61*, 3315–3319.
- (67) (a) Gehrhus, B.; Hitschcock, P. B.; Lappert, M. F. *Organometallics* **1997**, *16*, 4861–4864. (b) Gehrhus, B.; Lappert, M. F. *Polyhedron* **1998**, *17*, 999–1000.
- (68) Xiong, Y.; Yao, S.; Driess, M. *Chem. Eur. J.* **2009**, *15*, 8542–8547.

- (69) Denk, M.; Hayashi, R.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 10813–10814.
- (70) Kong, L.; Cui, C. *Organometallics* **2010**, *29*, 5738–5740.
- (71) Abe, T.; Iwamoto, T.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2006**, *128*, 4228–4229.
- (72) Ghadwal, R. S.; Sen, S. S.; Roesky, H. W.; Granitzka, M.; Kratzert, D.; Merkel, S.; Stalke, D. *Angew. Chem., Int. Ed.* **2010**, *49*, 3952–3955.
- (73) Sen, S. S.; Tavcar, G.; Roesky, H. W.; Kratzert, D.; Hey, J.; Stalke, D. *Organometallics* **2010**, *29*, 2343–2347.
- (74) Tavčar, G.; Sen, S. S.; Roesky, H. W.; Hey, J.; Kratzert, D.; Stalke, D. *Organometallics* **2010**, *29*, 3930–3935.
- (75) (a) Back, O.; Kuchenbeiser, G.; Donnadiou, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 5530–5533. (b) Back, O.; Donnadiou, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. *Nat. Chem.* **2010**, *2*, 369–373.
- (76) (a) Masuda, J.; Schoeller, W. W.; Donnadiou, B.; Bertrand, G. *J. Am. Chem. Soc.* **2007**, *129*, 14180–14181. (b) Masuda, J. D.; Schoeller, W. W.; Donnadiou, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 7052–7055.
- (77) Xiong, Y.; Yao, S.; Brym, M.; Driess, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4511–4513.
- (78) Xiong, Y.; Yao, S.; Bill, E.; Driess, M. *Inorg. Chem.* **2009**, *48*, 7522–7524.
- (79) Schoeller, W. W. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5273–5280.
- (80) Damrauer, R.; Pusede, S. E. *Organometallics* **2009**, *28*, 1289–1294.
- (81) Peng, Y.; Fan, H.; Zhu, H.; Roesky, H. W.; Magull, J.; Hughes, C. E. *Angew. Chem., Int. Ed.* **2004**, *43*, 3443–3445.
- (82) Xiong, Y.; Yao, S.; Driess, M. *J. Am. Chem. Soc.* **2009**, *131*, 7562–7563.
- (83) Xiong, Y.; Yao, S.; Driess, M. *Chem. Asian J.* **2010**, *5*, 322–327.
- (84) Xiong, Y.; Yao, S.; Mueller, R.; Kaupp, M.; Driess, M. *J. Am. Chem. Soc.* **2010**, *132*, 6912–6913.
- (85) Yao, S.; Xiong, Y.; Driess, M. *Chem. Eur. J.* **2010**, *16*, 1281–1288.
- (86) (a) Kipping, F. S.; Lloyd, L. L. *J. Chem. Soc.* **1901**, 449. (b) Corey, J. Y. Historical Overview and Comparison of Silicon with Carbon. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Vol. 1, Chapter 1, pp 1–56.
- (87) Drake, R.; Mackinnon, I.; Taylor, R. Recent advances in the chemistry of siloxane polymers and copolymers. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1998; Vol. 2, Part 3, Chapter 38, p 2217 and references cited therein.
- (88) Xiong, Y.; Yao, S.; Driess, M. *Dalton Trans.* **2010**, *39*, 9282–9287.
- (89) Iwasawa, T.; Hooley, R. J.; Rebek, J., Jr. *Science* **2007**, *317*, 493–496.
- (90) Xiong, Y.; Yao, S.; Driess, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 6642–6645.
- (91) Xiong, Y.; Yao, S.; Mueller, R.; Kaupp, M.; Driess, M. *Nat. Chem.* **2010**, *2*, 577–580.
- (92) Sander, W.; Schroeder, K.; Muthusamy, S.; Kirschfeld, A.; Kappert, W.; Boese, R.; Kraka, E.; Sosa, C.; Cremer, D. *J. Am. Chem. Soc.* **1997**, *119*, 7265–7270.
- (93) Gubelmann, M. H.; Williams, A. F. *Struct. Bonding (Berlin)* **1983**, *55*, 1–65.
- (94) Yao, S.; Xiong, Y.; Brym, M.; Driess, M. *Chem. Asian J.* **2008**, *3*, 113–118.
- (95) (a) Meltzer, A.; Präsang, C.; Milsmann, C.; Driess, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 3170–3173. (b) Meltzer, A.; Inoue, S.; Präsang, C.; Driess, M. *J. Am. Chem. Soc.* **2010**, *132*, 3038–3046. (c) Jungton, A.-K.; Meltzer, A.; Präsang, C.; Braun, T.; Driess, M. *Dalton Trans.* **2010**, *39*, 5436–5438.