Synthesis and Properties of the First Stable Silylene – Isocyanide Complexes

Nobuhiro Takeda,[a] Takashi Kajiwara,[a] Hiroyuki Suzuki,[b] Renji Okazaki,[b] and Norihiro Tokitoh*[a]

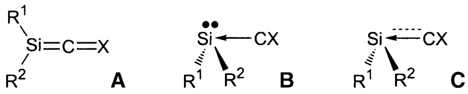
Abstract: The first stable silylene – isocyanide complexes, [Tbt(Mes)SiCNAr] (**5c**: Ar = Tip, **5d**: Ar = Tbt, **5e**: Ar = Mes*; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes = mesityl, Tip = 2,4,6-triisopropylphenyl, Mes* = 2,4,6-tri-*tert*-butylphenyl) were successfully synthesized by the reaction of a kinetically stabilized disilene, [Tbt(Mes)Si=Si(Mes)Tbt] (**1**), with bulky isocyanides, ArNC (**3c** – **e**). The spectroscopic data of **5c** – **e** and theoretical calculations for a model molecule indicated that **5c** – **e** are not classical cumulative compounds but the first stable silylene – Lewis base complexes. The reactions of **5c** – **e** with triethylsilane and 1,3-dienes gave the corresponding silylene adducts, and they underwent isocyanide-exchange reactions in the presence of another isocyanide at room temperature. These results indicate dissociation of complexes **5c** – **e** to the corresponding silylene **2** and isocyanides **3c** – **e** under very mild conditions. The reaction of **5c** with methanol gave the MeOH adduct **16**, [Tbt(Mes)SiHC(OMe)NTip], which has a hydrogen atom on the silicon atom. This regioselectivity can be explained in terms of the contribution of zwitterionic resonance structures **D** and **E**, which have an anion on the silicon atom. This result indicates that **5c** is not a classical cumulene having Si=C double bonds that should react with methanol to give adducts bearing a methoxyl group on the silicon atom. Although the reactions of **5c** – **e** with electrophilic reagents such as methanol, hydrogen chloride, and methyl iodide gave the formal silylene adducts, the studies on the reaction mechanism by trapping experiments and the observation of the intermediate suggested that the reaction mainly or partially proceeds by initial nucleophilic attack of the silicon atom, as is the case in the formation of **16** in the reaction of **5c** with methanol. It was revealed that **5c** – **e** show the nucleophilicity of the silicon atom, most likely resulting from the contribution of the zwitterionic resonance structures **D** and **E**.

Keywords: isocyanides · Lewis bases · silylenes · silacumulenes · silicon

Introduction

Recently, various types of compounds containing a stable double bond to silicon have been synthesized by taking advantage of the steric protection of bulky substituents.[1–4] On the other hand, the chemistry of compounds containing silicon as part of a cumulated double-bond system has been explored less, and only 1-silaallene has been structurally characterized as a stable compound.[5–7]

As for silaketenes, we can depict their structures as linear cumulenes **A** having two classical double bonds and nonlinear Lewis acid – base complexes **B**, where a Lewis base (CO) interacts with the vacant p orbital of a singlet silylene (Scheme 1). Silylene complexes with Lewis bases have also attracted much interest, however, they are too unstable to exist at ambient temperature and can be observed spectroscopically only in low-temperature matrices.[8] Since the chemistry of silaketenes contains many interesting subjects, the theoretical and experimental studies on their chemistry have been extensively performed. Ab initio calculations for H_2SiCO have predicted that the most stable structure is a nonlinear Lewis acid – base complex **B** ($H_2Si \leftarrow CO$) rather than a linear cumulene **A** ($H_2Si=C=O$).[9–11] Very recently, theoretical calculations at a much higher level of theory indicated that in structure **C**, partial π character in the Si–C bond may be a more appropriate description for H_2SiCO.[12] Experimentally, the reactions of silylenes, R^1R^2Si:, with carbon monoxide in low-temperature matrices have been



Scheme 1. Structure of R^1R^2SiCX (X = O, NR^3).

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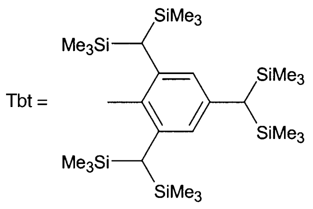
investigated by some groups.[13–15] It has been reported that the wavenumbers for the CO stretching vibration in the IR spectra of Me_2SiCO[14] and $(C_5H_5)_2SiCO$[13] are more consistent with the calculated wavenumbers for the linear structure **A** (AM1 or MNDO calculations) than those for the bent structure **B** (ab initio calculations with a 3–21G basis set). In contrast, West et al. have concluded that silylene–CO adducts such as Me_2SiCO and MesRSiCO (Mes = mesityl; R = Mes, *t*Bu, 2,6-*i*$Pr_2C_6H_3O$) are the Lewis acid–base complexes **B** with the pyramidal silicon atom, based on their UV/Vis spectra and chemical behavior.[15] In addition, Maier et al. have recently postulated that H_2SiCO has a pyramidal structure **B** on the basis of the comparison of experimental and calculated IR spectra.[9]

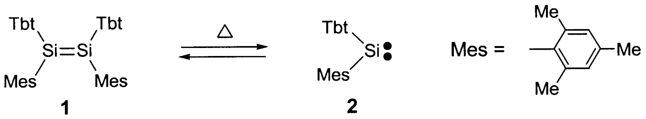
Although silaketenimines, which are isoelectronic with silaketenes, also attract much interest from the similar viewpoint to silaketenes, there have been only few examples of theoretical and experimental studies on silaketenimines. Very recently, Bharatam et al. carried out theoretical calculations on H_2SiCNH indicating a strong contribution from structure **C** in the resonance hybrid.[12] Experimentally, some transient silaketenimines have been proposed as an intermediate in the reactions of di-*t*butylsilylene with some isocyanides.[16, 17] The spectroscopic data for silaketenimines had not been fully understood until we started studying the kinetically stabilized systems. As for the tin analogues of silaketenimines, a stannnaketenimine, $[\{2,4,6\text{-}(CF_3)_3C_6H_2\}_2SnCNMes]$, has been isolated as a stable compound, and its X-ray structural analysis revealed that it has a bent SnCN structure bearing a pyramidally coordinated tin atom.[18] It has been proposed that the Sn–C bond in the SnCN structure, which was found to be longer than an Sn–C single bond, may be described as a double π-donor–acceptor interaction. Recently, Escudié et al. have reported the spectroscopic observation of two new species having an >MCE- (M = Group 14 element; E = Group 15 element) structure, for example, 1-phospha-3-silaallene [Tip(Ph)Si=C=PMes*] (Tip = 2,4,6-$(iPr)_3C_6H_2$; Mes* = 2,4,6-$(tBu)_3C_6H_2$)[19] and 1-phospha-3-germaallene [Mes_2Ge=C=PMes*].[20] These compounds have been found to represent allenic character in contrast to the stannaketenimine.

On the other hand, we have succeeded in synthesizing various low-coordination compounds containing heavier main-group elements[21] by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl (denoted Tbt hereafter).[22, 23] Recently, we reported the synthesis of the first stable silylene–isocyanide complexes, which are also the first stable Lewis-base complexes of a silylene, by the reaction of a disilene bearing Tbt groups and bulky isocyanides[24] and their reactions.[25–27] In these papers, we concluded that the silylene–isocyanide complexes have structure **B** based on their spectroscopic data and reactivity. Herein, we present the details of the synthesis and properties of the silylene–isocyanide complexes.



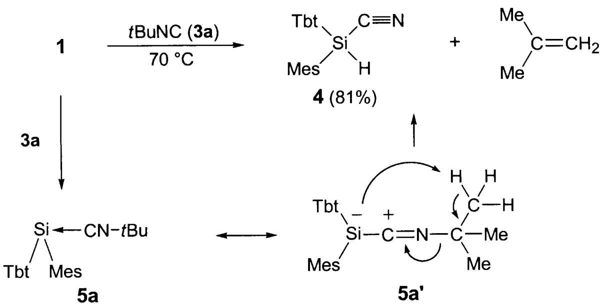
Results and Discussion

We have synthesized a hindered disilene **1** bearing Tbt and mesityl (Mes) groups and found that **1** is kinetically very stable but thermally labile, giving the corresponding silylene **2** under mild conditions (Scheme 2).[28–30] We investigated the synthesis of the desired silylene–isocyanide adducts by the reaction of **1** with some isocyanides bearing a bulky substituent, such as *t*Bu, Mes, 2,4,6-triisopropylphenyl (Tip), Tbt, and 2,4,6-tri-*tert*-butylphenyl (Mes*) groups.



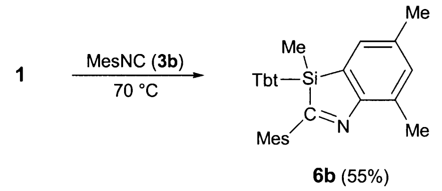
Scheme 2. The equilibrium between disilene **1** and silylene **2**.

Reaction of disilene 1 with isocyanides: The thermal reaction of disilene **1** with *tert*-butyl isocyanide (**3a**) at 70 °C resulted in the formation of cyanosilane **4** (81 %) together with isobutene (Scheme 3). The formation of **4** can be explained by the initial formation of silaylide **5a′**, followed by the proton-migration of the *t*Bu group accompanied with elimination of isobutene.



Scheme 3. Reaction of disilene **1** with *t*BuNC (**3a**).

Reaction of disilene **1** with mesityl isocyanide (**3b**),[31] which does not have a good leaving group such as isobutene, proceeded in a different way. When the suspended orange mixture of **1** and **3b** in THF was heated at 70 °C for 5 min, the reaction mixture turned dark green although the orange precipitates of bearly soluble disilene **1** still remained. Further heating for 30 min resulted in the color change of the solution to yellow, and the additional heating at 70 °C for 10 h finally afforded compound **6b** in 55 % yield (Scheme 4). The structure of **6b** was determined by NMR spectroscopy, high-resolution mass spectrometry, elemental analysis, and X-ray crystallographic analysis (Figure 1). The formation of **6b** was rationalized by the explanation described below. The initially formed silylene–isocyanide complex **5b** undergoes nucleo



Scheme 4. Reaction of disilene **1** with MesNC (**3b**).

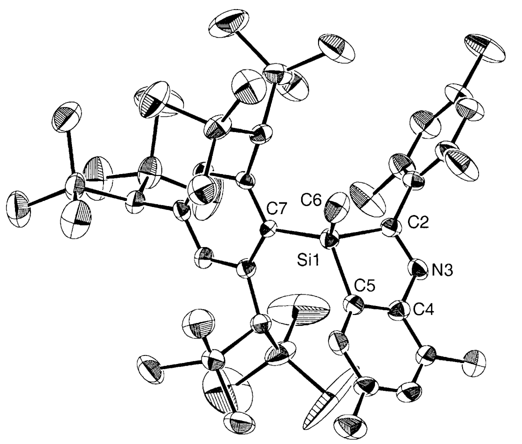


Figure 1. Structure of **6b** (ORTEP drawing with thermal ellipsoid plots, 30% probability for non-hydrogen atoms; hydrogen atoms omitted for clarity).

philic attack of the silicon atom at the *o*-position of the mesityl group and the successive migration of the mesityl and methyl groups to afford **6b** (Scheme 5).

To confirm the formation of **5b**, the reaction of **1** with **3b** in C_6D_6 was monitored by NMR spectroscopy. When the reaction mixture was heated at 60 °C for 30 min, a blue suspension was obtained. The ^{29}Si and ^{13}C NMR spectra of the reaction mixture showed signals at $\delta = -69.2$ and 200.1 ppm, respectively, together with those of **1**. These characteristic signals in the ^{29}Si and ^{13}C NMR spectra arise from the corresponding silylene–isocyanide complex **5b**. Detailed discussion about the NMR chemical shifts of the silylene–isocyanide complexes **5** will be described later. Further heating led to the disappearance of the signals for **5b** and the appearance of those for compound **6b**.

In the reaction of disilene **1** with isocyanide **3b**, the intermediate **5b** is considered to undergo gradual conversion into **6b** because the nucleophilic silicon atom of **5b** readily attacks the *o*-carbon atom of the mesityl group under the conditions of this reaction. To prevent this attack of the silicon atom, we examined the reactions of **1** with some isocyanides bearing a bulky substituent such as Tip, Tbt, and Mes*.

Tbt-substituted isocyanide **3d** was synthesized by dehydration of the corresponding formamide (TbtNHCHO) (**7**) with phosphorus oxychloride and diisopropylamine in CH_2Cl_2 as in the case of TipNC (**3c**).[32] Formamide **7** was synthesized by the treatment of aniline ($TbtNH_2$)[22] with a mixed anhydride prepared from formic acid and acetic anhydride. The structure of **3d** was definitively determined by X-ray structural analysis (Figure 2). The structural analysis showed the linear structure of the C1-N2-C3 unit (178.6(2)°) and the C1–N2 bond with a high bond order close to a triple bond, and suggested the sp hybridization of the C1 and N2 atoms. These values are similar to those of reported isocyanides.[33–36]

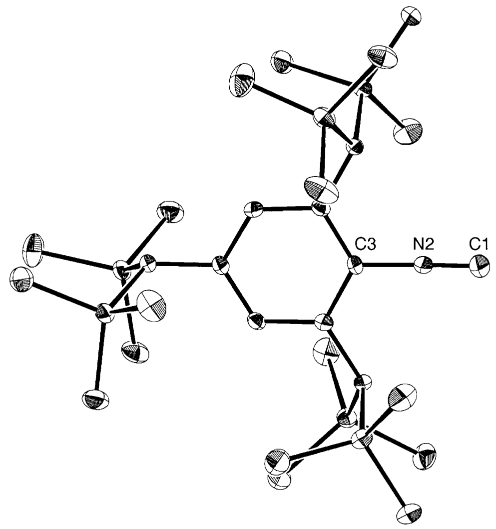
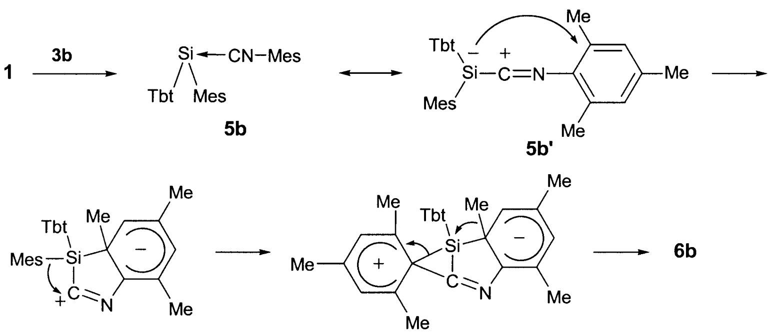
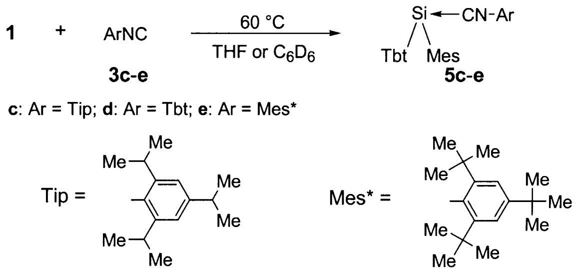


Figure 2. Structure of **3d** (ORTEP drawing with thermal ellipsoid plots, 50% probability for non-hydrogen atoms; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]; C1–N2 1.158(3), N2–C3 1.404(2); C1-N2-C3 178.6(2).

When a THF or C_6D_6 suspension of disilene **1** and an isocyanide substituted by Tip (**3c**),[32] Tbt (**3d**), or Mes* (**3e**)[37] was heated in a sealed tube at 60 °C for several minutes, the original orange suspension changed into a bluish green (**5c**), greenish blue (**5d**) or deep blue (**5e**) solution, respectively. Further heating at the same temperature for 2 h (**5c**) or for 6 h (**5d** and **5e**) resulted in the almost quantitative formation of the corresponding silylene–isocyanide adducts **5c–e**, which were fully characterized by their ^{1}H, ^{13}C, and ^{29}Si NMR spectra (Scheme 6). Slow evaporation of the solvent from the reaction solution gave bluish green (**5c**), greenish blue (**5d**) or deep blue (**5e**) powders, but crystals of **5c–e** suitable for X-ray crystallographic analysis have not been obtained so far. These adducts **5c–e** are stable



Scheme 5. Plausible mechanism for the formation of **6b**.



Scheme 6. Synthesis of silylene – isocyanide complexes **5c** – **e**.

in solution at 60 °C for several hours under an argon atmosphere, although they are extremely sensitive to moisture.

Spectral features of silylene – isocyanide complexes 5c – e: The ^{29}Si NMR spectra of **5c** – **e** showed signals at much higher field ($\delta = -53.6$ for **5c**, -57.4 for **5d**, and -48.6 ppm for **5e**) (Table 1) than those of silaallene ($\delta = 48.4$ ppm),[6] 1-phospha-3-silaallene ($\delta = 75.7$ ppm),[19] and silenes ($\delta = 41 - 144$ ppm) having an sp^2 silicon,[1] indicating that the Si–C bonds of the SiCN units in **5c** – **e** are electronically very different from other low-coordinate silicon species. It is strongly suggested that the Si–C bonds of the SiCN units are not double bonds, although we can not rule out the possibility that the Si–C bonds are a novel type of double bond such as in structure **C**. Moreover, almost the same ^{29}Si chemical shifts in THF as those in C_6D_6 (Table 1) strongly suggest the absence of any interaction between **5c** – **e** and THF.

Table 1. ^{29}Si and ^{13}C NMR (for the SiCN Unit) and UV/Vis spectra of **5c** – **e**.

	^{29}Si NMR [δ] C_6D_6	^{29}Si NMR [δ] THF	^{13}C NMR [δ] C_6D_6	$^{1}J_{Si,C}$ [Hz] C_6D_6	UV/Vis [nm] (ε) THF
5c: Ar = Tip	-53.6	-55.7	209.2	38.6	596 (400)
5d: Ar = Tbt	-57.4	-57.9	196.6	22.1	397 (3000) 632 (100)
5e: Ar = Mes*	-48.6	-48.9	178.5	1.0	390 (2000) 671 (200)

The ^{13}C NMR signals of **5c** – **e** appeared at slightly lower or similar field ($\delta = 209.2$ for **5c**, 196.6 for **5d**, and 178.5 ppm for **5e** in C_6D_6) compared with those of the corresponding free isocyanides ($\delta = 171.7$ for **3c**, 170.0 for **3d**, and 178.6 ppm for **3e** in C_6D_6).

To determine the $^{1}J_{C,Si}$ couplings accurately, we examined the synthesis of ^{13}C-labeled isocyanides. A ^{13}C nucleus was introduced by using commercially available formic acid with 99% ^{13}C enrichment in the preparation of ^{13}C-labeled formamides ArNH^{13}CHO (^{13}C-**6c**: Ar = Tip; ^{13}C-**6d**: Ar = Tbt; ^{13}C-**6e**: Ar = Mes*).[38] ^{13}C-Labeled isocyanides ^{13}C-**3c** – **e** were prepared from ^{13}C-**6c** – **e** by a method similar to that used in the synthesis of unlabeled **3c** – **e**. The coupling constants for the Si–C bonds of the SiCN unit, $^{1}J_{Si,C}$, could be determined by the ^{29}Si NMR spectra of the ^{13}C-labeled silylene – isocyanide complexes ^{13}C-**5c** – **e**. These were prepared by the reaction of **1** with the ^{13}C-labeled isocyanides ^{13}C **3c** – **e** in C_6D_6. The $^{1}J_{Si,C}$ values for **5c** – **e** (Table 1) with the order of **5c** > **5d** > **5e** are smaller than the coupling constants for the Si–C single bonds (50 Hz for Me$_4$Si)[39, 40] and the Si=C double bonds (83 – 85 Hz).[41] The small $^{1}J_{Si,C}$ values are known to indicate long Si–C bond lengths and/or the small s character of the Si–C bond, both of which lead to weak Si–C bonds. Therefore, these results strongly suggest that the Si–C bonds of the SiCN units are considerably weak and their strength decreases in the order **5c** > **5d** > **5e** with increasing bulkiness of the substituents.

In the UV/Vis spectra of **5c** – **e**, the absorption maxima were observed around 600 to 670 nm (Table 1) as in the case of a silylene – ketone complex.[42] These results suggest that **5c** – **e** are not cumulenes **A** but silylene – isocyanide complexes **B**.

Raman spectra of **5c** – **e** showed absorption bands at 2002 (**5c**), 1919 (**5d**), and 1996 cm^{-1} (**5e**), respectively, which are assigned to the C–N stretches of the SiCN units. These values are smaller than those for the corresponding isocyanides (2113 cm^{-1} for **3c**, 2108 cm^{-1} for **3d**, and 2119 cm^{-1} for **3e**).

Thus, it can be concluded that **5c** – **e** are not classical cumulenes but silylene – isocyanide complexes based on their ^{29}Si NMR chemical shifts, $^{1}J_{Si,C}$ values, and the absorption maxima in the UV/Vis spectra. In addition, **5c** – **e** can be represented as Lewis acid (silylene **2**) – Lewis base (isocyanide) complexes. Silylene – Lewis base complexes have been known to dissociate readily into the corresponding free silylenes by annealing the matrices, giving the disilene or oligosilane,[8] therefore, it is notable that **5c** – **e** are the first examples for silylene – Lewis base complexes stable at room temperature.

Theoretical calculation for a silylene – isocyanide complex: The results of spectroscopic studies described above are further supported by the theoretical calculations[43] of [(Dmp)$_2$SiCN(Dmp)] (**5f**) (Dmp = 2,6-dimethylphenyl) as well as the theoretical calculation for Ph$_2$SiCNPh[24]. The structural optimization at the B3LYP/6 – 31G(d) level clearly showed that **5f** is a silylene – Lewis base complex with a bent Si1–C2–N3 bond (159.3°) and a pyramidal structure around the central silicon atom (Figure 3). The Si1–C2 length (1.867 Å) is comparable to a Si–C single bond length (typical

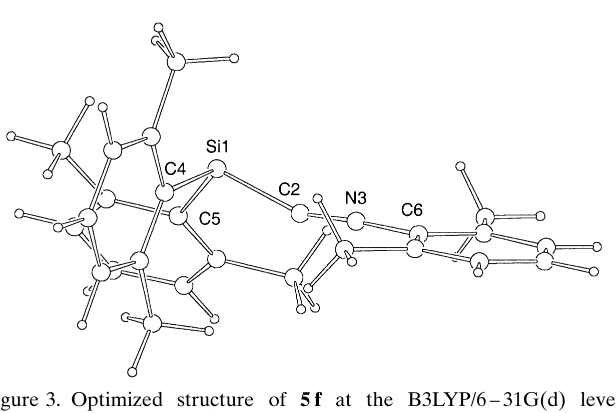
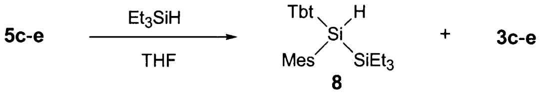


Figure 3. Optimized structure of **5f** at the B3LYP/6 – 31G(d) level. Selective bond lengths [Å] and bond angles [°]: Si1–C2 1.867, Si1–C4 1.945, Si1–C5 1.918, C2–N3 1.184, N3–C6 1.373; Si1-C2-N3 159.35, C2-Si1-C4 94.12, C2-Si1-C5 110.43, C4-Si1-C5 111.41, C2-N3-C6 175.00.

values for Si$-$C$_{sp}$, Si$-$C$_{ar}$, and Si$-$C$_{sp^3}$ lengths: 1.837, 1.868, and 1.863 Å),[44] and the C2$-$N3 length (1.184 Å) is almost the same as the calculated C$-$N bond length of DmpNC (1.182 Å). The chemical shifts of the Si and C atoms in the SiCN unit calculated at the GIAO-B3LYP level (6–311G(3d) for Si and 6–311G(d) for C, N, and H) were $\delta = -78.9$ and 186.5 ppm, respectively. These values are comparable with those of the observed values shown in Table 1. Moreover, the calculated vibrational frequency of **5f** assigned to the C$-$N stretching vibration (2078 cm^{-1}, computed at the B3LYP/6–31G(d) level and scaled by 0.96)[45] is smaller than the calculated value for the C$-$N stretching of DmpNC (2110 cm^{-1}). This tendency is consistent with that of the experimental values for the Raman shifts of **5c**–**e** described above. The fact that the results obtained by theoretical calculations are in good agreement with the experimental data suggests that the structures of **5c**–**e** might be similar to the calculated structure for [(Dmp)$_2$SiCN(Dmp)].

Reactions with triethylsilane: The silylene–isocyanide complexes **5c**–**e** reacted with triethylsilane at room temperature to give the silylene adduct **8** in the yields of 66, 86, and 69%, respectively, along with the corresponding isocyanides **3c**–**e** (Scheme 7).



	8	3c-e
c: 50 °C, 28 h	66%	42%
d: RT, 17 d	86%	94%
e: RT, 41 h	69%	98%

Scheme 7. Reaction of silylene–isocyanide complexes **5c**–**e** with Et$_3$SiH.

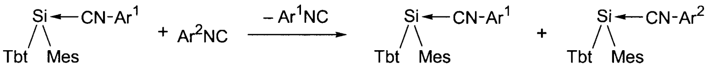
These results clearly indicate that **5c**–**e** dissociate into **2** and **3c**–**e** in solution and an equilibrium exists between them. Grützmacher et al. have reported[18] that a stannaketenimine dissociates into the corresponding stannylene and isocyanide and that the variable-temperature ^{117}Sn NMR experiments show a downfield shift with increasing temperature owing to an increase of the ratio of the stannylene in the equilibrium mixture. This result suggests rapid interconversion between the stannaketenimine and the stannylene plus isocyanide. In contrast, the ^{29}Si and ^{13}C chemical shifts of **5c**–**e** at 7, 25, and 60 °C were almost the same (Table 2). Moreover, the reaction of **1** with an excess amount of **5c**–**e** resulted in the observation of separate signals of **3c**–**e** and **5c**–**e** in the ^{1}H and ^{13}C NMR spectra at room temperature. These findings indicate that the rate of interconversion between **5c**–**e** and **2** plus **3c**–**e** is very slow on the NMR time scale and that the ratio of **2** in the equilibrium mixture is too small to be observed by NMR spectroscopy.

Table 2. ^{29}Si and ^{13}C NMR (for the SiCN Unit) chemical shifts [δ] of **5c**–**e** in C$_6$D$_6$.

	5c: Ar = Tip		**5d**: Ar = Tbt		**5e**: Ar = Mes*	
	^{29}Si NMR	^{13}C NMR	^{29}Si NMR	^{13}C NMR	^{29}Si NMR	^{13}C NMR
7 °C	–53.9	209.1	–57.8	196.5	–49.0	177.5
25 °C	–53.6	209.2	–57.4	196.6	–48.6	178.5
60 °C	–53.2	209.3	–56.5	196.6	–47.9	179.1

In the above trapping reactions with triethylsilane, the reaction rates became larger in the order **5c** < **5d** < **5e** with increasing bulkiness of the substituents. This tendency can be explained by the fact that the larger the substituent, the larger the steric repulsion between it and the Tbt group, thus increasing the rate of the dissociation of **5c**–**e** into silylene **2**. This result is consistent with the correlation between congestion of the substituents and strength of the Si$-$C bond suggested by the $^1J_{Si,C}$ values of the SiCN unit.

Isocyanide exchange reaction: To obtain further evidence for the equilibrium between silylene–isocyanide complexes **5c**–**e** and silylene **2** plus isocyanides **3c**–**e**, we examined the isocyanide exchange reactions of **5c**–**e**. When a C$_6$D$_6$ solution of Mes*-substituted silylene–isocyanide complex **5e** was added to Tbt-substituted isocyanide **3d** at room temperature, the original deep blue solution quickly turned greenish blue. The ^{1}H and ^{29}Si NMR spectra showed the formation of Tbt-substituted silylene–isocyanide complex **5d** with a ratio of **5e**:**5d** = 1:5 together with a free isocyanide **3e** (Scheme 8).



Ar^1 = Mes* (**5e**), Ar^2 = Tbt (**3d**)	1	:	5
Ar^1 = Tbt (**5d**), Ar^2 = Tip (**3c**)	1	:	5

Scheme 8. Isocyanide-exchange reaction.

The mechanism of the isocyanide exchange reaction was interpreted reasonably in terms of the initial dissociation of **5e** into **2** and **3e** and the subsequent complexation of **2** with **3d** giving **5d**.

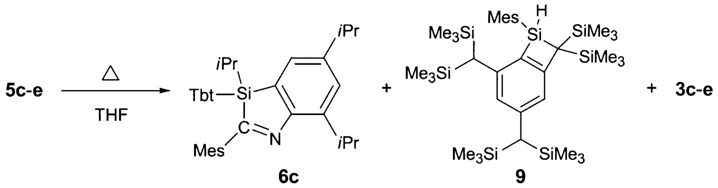
In addition, the reaction of **5d** with Tip-substituted isocyanide **3c** in C$_6$D$_6$ at room temperature was examined. The color of the solution changed from greenish blue to bluish green, and the ^{1}H and ^{29}Si NMR spectra indicated the formation of **5c** with the ratio of **5d**:**5c** = 1:5 (Scheme 8).

These results clearly indicate the equilibrium between **5c**–**e** and **2** plus **3c**–**e**. Moreover, the equilibrium ratio of **5c**–**e** to **3c**–**e** are consistent with the spectral and structural features described in the previous sections, that is, the strength of the coordination of an isocyanide in a silylene–isocyanide complex increases in the order **5e** < **5d** < **5c** with decreasing bulkiness of the substituents.

The results described here indicate the possibility of synthesizing less hindered silylene–Lewis base complexes even at room temperature by utilizing this Lewis base exchange reaction. By the use of this method we examined the synthesis of Mes-substituted silylene–isocyanide complex **5b**, which is unstable at 60 °C (vide supra). When a C$_6$D$_6$ solution of **5e** was added to **3b**, the original deep blue solution turned green. The ^{29}Si and ^{13}C NMR spectra showed characteristic peaks at $\delta = -69.2$ and 200.1 ppm, respectively, which are identical to those observed in the reaction of **1** with **3b**. These chemical shifts are close to those of other silylene–isocyanide complexes **5c**–**e**, and assigned to those of **5b**. The

UV/Vis absorption spectrum of **5b** in THF showed the absorption maximum at 599 nm as in the case of other silylene – isocyanide complexes **5c – e**. Although the formation of a marginally stable silylene – isocyanide complex **5b** was confirmed, the full assignment of the NMR spectra could not be achieved due to the gradual decomposition of **5b** into a complicated mixture even at room temperature.

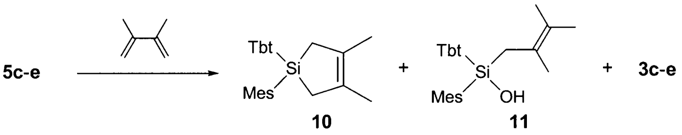
Thermolysis: When complex **5c** was heated at 80 °C for 22 h, the bluish green color of **5c** disappeared to give compound **6c** (37 %) together with a small amount of isocyanide **3c** (3 %) (Scheme 9). The structure of **6c** was determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectra and a high-resolution FAB mass spectrum, and the assignment of the NMR spectra was performed by the use of 2D NMR technique. Compound **6c** is considered to be formed by the same mechanism as that for **6b** in the reaction of silylene **2** with mesityl isocyanide **3b** (Scheme 5).



	6c	9	3c-e
c: 80 °C, 22 h	37%	–	3%
d: 100 °C, 2 d	–	65%	85%
e: 100 °C, 9 h	–	78%	94%

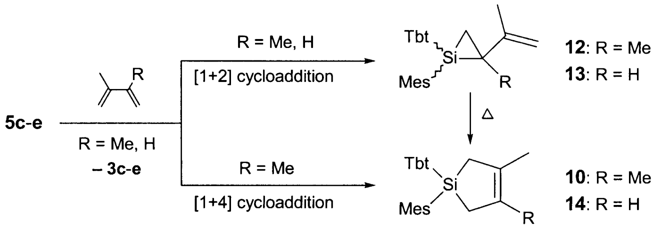
Scheme 9. Thermolysis of silylene – isocyanide complexes **5c – e**.

In contrast, thermolysis of complexes **5d** and **5e** at 100 °C gave benzo-1-silacyclobutene **9** in yields of 65 % (**5d**) and 78 % (**5e**) together with the corresponding isocyanides **3d** (85 %) and **3e** (94 %), respectively (Scheme 9). Since compound **9** has been reported to be formed in the thermolysis of disilene **1** by means of intermediary silylene **2** in the absence of a trapping reagent,[28, 29] **5d** and **5e** probably undergo the dissociation to silylene **2** in this reaction. In contrast to the less hindered system **5c**, the extremely bulky Tbt and Mes* groups in **5d** and **5e** may prevent the nucleophilic attack of the silicon atom to the *o*-positions of the Tbt and Mes* groups and accelerate the dissociation of **5d** and **5e** to **2** plus **3d** and **3e**.



	10	11	3c-e
c: 50 °C, 97 h	49%	15%	58%
d: RT, 106 h	33%	39%	92%
e: RT, 71 h	34%	47%	100%

Scheme 10. Reaction of silylene – isocyanide complexes **5c – e** with 2,3-dimethyl-1,4-butadiene.



Scheme 11. Mechanism for the reaction of silylene – isocyanide complexes **5c – e** with dienes.

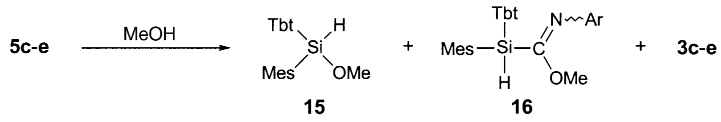
Reactions with 2,3-dimethyl-1,3-butadiene: Reaction of **5c – e** with 2,3-dimethyl-1,3-butadiene gave the [1+4] cycloadduct **10** with silylene **2** (**c**: 49 %, **d**: 33 %, **e**: 34 %) and compound **11** (**c**: 15 %, **d**: 39 %, **e**: 47 %) together with the corresponding isocyanides **3c – e** (**c**: 58 %, **d**: 92 %, **e**: 100 %) (Scheme 10). Since the reaction of disilene **1** with 2,3-dimethyl-1,3-butadiene also gives **10** and **11**, passing through silylene **2**,[28] it is considered that these reactions also proceed by dissociation to silylene **2** and the corresponding free isocyanides **3c – e**. The formation of **11** is probably interpreted in terms of hydrolysis of the [1+2] cycloadduct **12** during separation (Scheme 11), and this mechanism was supported by the reaction of **5e** with isoprene giving the corresponding vinylsilirane **13** (89 %), which was fully characterized by NMR spectroscopy[26] (Scheme 11). The reaction rates increased in the order of **5c** < **5d** < **5e**, which can be rationalized by an explanation similar to that for the reaction with triethylsilane; the reaction is accelerated by the introduction of the bulkier substituent which leads to the easier dissociation of **5c – e** into **2** and **3c – e**.

To investigate the mechanism for the reaction of complexes **5c – e** with 2,3-dimethyl-1,3-butadiene, the reaction of **5e** was monitored by ^{29}Si NMR spectroscopy.[26] When complex **5e** was allowed to react with 2,3-dimethyl-1,3-butadiene in C_6D_6 in a sealed tube at room temperature for 2.5 h, the deep blue solution of **5e** turned greenish yellow. The ^{29}Si NMR spectrum showed three peaks ($\delta = -76.3$, -72.9, and -5.3 ppm with the peak height ratio of approximately 2:6:3) besides the peaks for trimethylsilyl groups. The peak at $\delta = -5.3$ was assigned to that for the [1+4] cycloadduct **10**, and the peaks at $\delta = -76.3$, -72.9 ppm were attributed to the geometric isomers of [1+2] cycloadducts **12**. After heating the reaction mixture at 50 °C for 7 h, no change was observed in the ^{29}Si NMR spectrum. Further heating at 100 °C for 5 h led to the disappearance of the signals for **12**, only **10** (60 %, isolated yield) being observed. This result suggests that silylene **2** undergoes both the [1+2] and [1+4] cycloaddition to 2,3-dimethyl-1,3-butadiene at the initial stage of this reaction.

In contrast to this result, the formation of a silolene by the reaction of dimethylsilylene with 1,3-dienes is considered to proceed by an initial 1,2-addition forming a vinylsilirane followed by its non-concerted rearrangement.[46, 47] Silolene **14** in fact was formed in good yields by thermolysis of the vinylsilirane **13** obtained by the above-mentioned reaction of **5e** with isoprene.[26]

The occurrence of the direct [1+4] cycloaddition in the reaction of **5c – e** with 2,3-dimethyl-1,3-butadiene is most likely due to the severe steric repulsion between the methyl group of the butadiene and the bulky substituents on the silicon of **5c – e**, which hinders the [1+2] cycloaddition and hence favors the direct [1+4] cycloaddition.

Reaction with methanol: When methanol was added to a THF solution of the silylene – isocyanide complex **5c** at room temperature, the bluish green color of the solution disappeared immediately to give **15** (70%) and **16c** (7%) along with **3c** (54%) (Scheme 12). The reaction at low temperature afforded **16c** (40%) as the main product together with **15** (10%) and **3c** (20%).



	15	16	3c-e
c: RT, ca 5 min	70%	7%	54%
−78 °C ~ 0 °C	10%	40%	20%
d: RT, ca 5 min	86%	–	91%
−78 °C ~ 7 °C	78%	–	94%
e: RT, ca.5 min	75%	–	98%

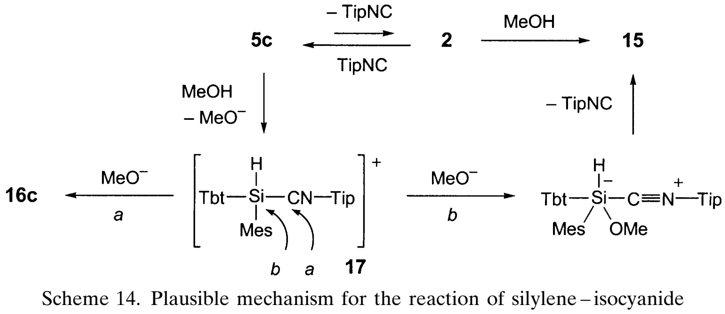
Scheme 12. Reaction of silylene–isocyanide complexes **5c–e** with MeOH.

Interestingly, the 1,2-adduct **16c** has a methoxyl group on the carbon atom. This regioselectivity is in a sharp contrast to that of the 1,2-addition of methanol to the Si=C double bonds of silenes, a metastable 1-phospha-3-silaallene, and transient 1-silaallenes, where a methoxyl group was attached to the silicon atom.[1, 19] This selectivity is similar to that in ketenimines, and it seems that **5c** has a Si=C double bond with "reversed polarity".[6, 48, 49] However, this reactivity can be reasonably explained in terms of the contribution of the zwitterionic resonance structures **D** and **E**, which have an anion on the silicon atom as shown in Scheme 13. Such an interpretation is consistent with the spectroscopic data of **5c** such as an upfield shift in the ^{29}Si NMR and the small $^{1}J_{\mathrm{Si,C}}$ values.

D **E**

Scheme 13. Resonance structures of $R^1R^2SiCNR^3$.

The formation of **15** and **16c** in the reaction of **5c** with methanol can be interpreted in terms of the initial protonation of the silicon atom of **5c** by methanol followed by an attack of MeO^- (or MeOH) on the carbon (path *a*) or silicon (path *b*) atom in the SiCN unit (Scheme 14). Path *a* leads to the production of **16c**, while path *b* results in the formation of **15**, which is likely to be partially formed also by the reaction of methanol with silylene **2** generated by dissociation of **5c**. The higher yield of **15** in the reaction at room temperature compared with the reaction at low temperature is probably due to the increase in the equilibrium ratio of **2** at the higher temperature.

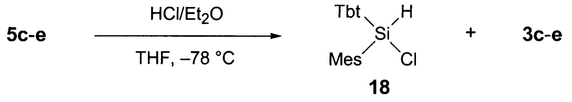


Scheme 14. Plausible mechanism for the reaction of silylene–isocyanide complexes **5c–e** with methanol.

In the reaction of **5d** or **5e** with methanol at room temperature, **15** was obtained in the yield of 86 or 75%, respectively, together with **3** (**d**: 91%, **e**: 98%) without production of **16d** or **16e** (Scheme 12). In addition, the reaction of **5d** at low temperature did not give **16d**. These reactions are also explained by the same mechanism as in the case of **5c** (Scheme 14). The sole formation of **15** is most likely due to the higher congestion of Tbt and Mes* groups than the Tip group attached to the nitrogen atom, which disturbs the attack of MeO^- (or MeOH) to the carbon atom in the SiCN unit (path *a*) and makes the equilibrium between **5** and **2** plus **3** shift into the silylene side.

To confirm the above reaction mechanism shown in Scheme 14, the reaction of **5e** with sodium methoxide in THF was monitored by ^{29}Si NMR spectroscopy. In contrast to the rapid reaction of **5e** with methanol, when the reaction mixture was left at room temperature for 6 h there was no change in the ^{29}Si NMR spectrum. This result strongly suggests that the first step in the reaction of **5e** with methanol is not the attack of methoxide anion at the silicon or carbon atom of **5e** (Scheme 14).

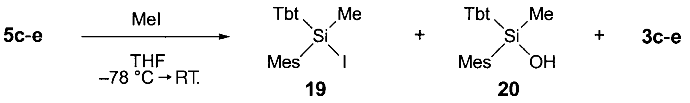
Reaction with HCl: When the complexes **5c–e** were treated at −78 °C with solution of hydrogen chloride in diethyl ether, which is a very reactive electrophilic reagent, the color of **5c–e** quickly disappeared to give chlorosilane **18** (**c**: 41%, **d**: 75%, **e**: 75%) together with the corresponding isocyanides **3c–e** (**c**: 43%, **d**: 92%, **e**: 90%) (Scheme 15). This rapid formation of **18** and **3c–e** may also be explained by a mechanism similar to that for the reaction with methanol (Scheme 14).



	18	3c-e
c:	41%	43%
d:	75%	92%
e:	75%	90%

Scheme 15. Reaction of silylene–isocyanide complexes **5c–e** with HCl.

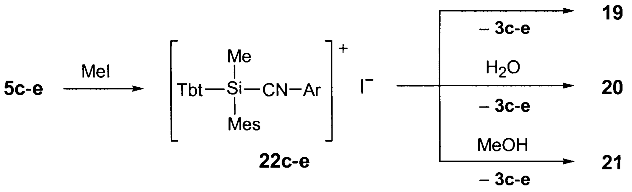
Reaction with methyl iodide: To investigate the nucleophilic character of the complexes **5c–e**, the reactions of **5c–e** with another electrophile were examined. When **5c–e** were treated with methyl iodide at −78 °C and the mixture gradually warmed, the color of **5c–e** disappeared at −40 °C for **5c**, at 25 °C for **5d**, and at −20 °C for **5e**. The separation of the crude products after warming the reaction mixture to room temperature afforded iodosilane **19** (**a**: 16%, **b**: 29%, **c**: 19%) and silanol **20** (**c**: 20%, **d**: 17%, **e**: 18%) along with the corresponding isocyanides **3c–e** (**c**: 28%, **d**: 98%, **e**: 97%) (Scheme 16).



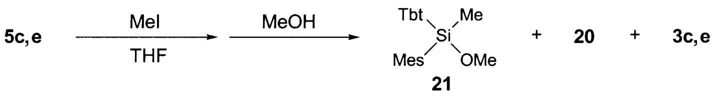
	19	20	3c-e
c:	16%	20%	28%
d:	29%	17%	98%
e:	19%	18%	97%

Scheme 16. Reaction of silylene–isocyanide complexes **5c–e** with MeI.

Since **19** is not sensitive to moisture and the ^{1}H NMR spectrum of the crude products showed the existence of **20** before the separation, the formation of **20** suggests the reaction mechanism involving the ionic intermediates **22c–e**, which are analogous to **17** in the reaction with methanol (Scheme 14). Since the formation of **20** implies that the intermediates **22c–e** have a lifetime long enough to be trapped by H_2O during separation (Scheme 17), the trapping experiments of **22c** and **22e** by methanol were examined. When methyl iodide was added to a solution of the complex **5c** in THF at $-78\,^\circ$C and the reaction mixture warmed to $-50\,^\circ$C, the original bluish green solution turned orange. Addition of methanol to this solution resulted in the formation of **21** in 29% yield together with **3c** (13%) (Scheme 18). A similar trapping experiment in the reaction of **5e** with methyl iodide also gave **21** (18%), **20** (14%), and **3e** (90%). Since the reaction of iodosilane **19** with methanol leading to **21** was found to be very slow under the conditions similar to those for the trapping experiments, the formation of **21** in the trapping experiments is explained in terms of the reaction of the intermediate **22c** or **22e** with methanol (Scheme 17). Of course, **19** may be partially yielded by the reaction of methyl iodide with silylene **2** generated by dissociation of **5c–e**.



Scheme 17. Plausible mechanism for the reaction of silylene–isocyanide complexes **5c–e** with MeI.

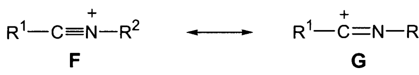


MeI, THF	MeOH	21	20	3c,e
c: –78 °C → –50 °C	–50 °C → RT.	29%	–	13%
e: –78 °C → –20 °C	–20 °C → RT.	18%	14%	90%

Scheme 18. Trapping reaction of the intermediate in the reaction of silylene–isocyanide complexes **5c–e** with MeI.

To observe the intermediate **22e**, the reaction of **5e** with methyl iodide was monitored by NMR spectroscopy. The ^{29}Si NMR spectrum of the reaction mixture at $-10\,^\circ$C showed signals that may be assigned to **22e** at $\delta=-10.0$ and -9.8 ppm (the ratio of peak heights is ca. 7:3). The observation of the two signals indicates the existence of two rotational isomers probably due to the restricted rotation involving the Si–C(Tbt) and/or Si–C(Mes) bonds at low temperature. These signals disappeared on warming to room temperature and iodosilane **19** and isocyanide **3e** were obtained in the yields of 42 and 94%, respectively. Since the ^{13}C NMR signals for **22e** could not be assigned in the above experiment, the reaction of a ^{13}C-labeled complex ^{13}C-**5e** with methyl iodide was examined. The ^{13}C NMR spectrum of this reaction mixture at $-10\,^\circ$C exhibited two peaks at $\delta=132.9$ and 133.2 ppm (the ratio of the peak heights is ca. 7:3) as the only peaks for the labeled ^{13}C besides that of isocyanide **5e**. The ^{29}Si NMR spectrum showed two sets of characteristic doublets at $\delta=-10.0$ ppm ($^1J_{\mathrm{Si,C}}=22$ Hz) and at $\delta=-9.8$ ppm ($^1J_{\mathrm{Si,C}}=23$ Hz), and these chemical shifts are the same as those of nonlabeled **22e**. These signals in the ^{13}C and ^{29}Si NMR spectra, which disappeared on warming to room temperature, were assigned to those for the ^{13}C-labeled intermediate ^{13}C-**22e**.

Since carbocations[50] and silyl cations[51] are known to show downfield shifts in the ^{13}C and ^{29}Si NMR spectra, respectively, a positive charge probably localizes neither on the carbon atom nor on the silicon atom. Moreover, the ^{13}C NMR chemical shifts are close to those of reported $[R_3C{-}CNR]^+$,[52] which are depicted as structure **F** with a positive charge on the nitrogen atom as shown in Scheme 19. It is therefore considered that resonance structure **F** makes a large contribution to the structure of the intermediate **22e**. The coupling constants in the Si–C bond of the SiCN unit (22–23 Hz) were much larger than that of the corresponding silylene complex **5e** (1.0 Hz), suggesting that the corresponding trivalent silicon cation (silylium ion)[51] is more strongly coordinated by the Lewis base, isocyanide **3e**, than silylene **2**.



$$\underset{\mathbf{F}}{R^1{-}C{\equiv}\overset{+}{N}{-}R^2} \longleftrightarrow \underset{\mathbf{G}}{R^1{-}\overset{+}{C}{=}N{-}R^2}$$

Scheme 19. Resonance structures of $[R^1CNR^2]^+$.

Thus, the initial attack of the electrophilic center of methyl iodide to the silicon atom of the complexes **5c–e** was confirmed by the trapping experiments and observation of the intermediate ^{13}C-**22e** by ^{13}C and ^{29}Si NMR spectroscopy.

Conclusion

We succeeded in the synthesis of the first stable silylene–isocyanide complexes **5c–e** by taking advantage of an effective steric protecting group, Tbt. Investigations of their spectroscopic properties and theoretical calculations led to the conclusion that **5c–e** are not classical cumulative compounds **A** but the first stable silylene–Lewis base complexes **B**. The complexes **5c–e** dissociated into silylene **2** and the corresponding isocyanides **3c–e** under mild conditions, such as at room temperature. The reactions of **5c–e** with triethylsilane and 1,3-dienes gave the corresponding silylene adducts, and the isocyanide exchange reaction occurred at room temperature. These reactivities indicate that **5c–e** behaved as silylene equivalents. In addition, the high nucleophilicity of the silicon atom was shown in the reaction with methanol, hydrogen chloride, and methyl iodide. Especially, the reaction of **5c** with methanol gave the corresponding adduct **16**, which was probably formed by the initial protonation of the silicon atom followed by the attack of methoxide anion to the carbon atom of the SiCN moiety. This regioselectivity is in sharp contrast to that in the addition of methanol to the usual Si=C double bonds, which gives the adducts bearing methoxyl group on the silicon atom. These facts can be interpreted in terms of the contribution of zwitterionic resonance structures **D** and **E**, which have an anion on the silicon atom.

These properties of **5c–e** resemble those of the reported stannaketenimine,[18] and indicate sharp contrasts to those of 1-phospha-3-silaallene[19] and 1-phospha-3-germaallene,[20] which reportedly have cumulative-compound character.

In view of the unique reactivities of the complexes **5c–e**, that is, 1) the high reactivity to electrophiles and 2) the dissociation into a silylene under mild conditions, applications of **5c–e** to the synthesis of new silicon containing species and the investigations on the reaction mechanism are attractive subjects in the future study.

Experimental Section

General procedure: All reactions were carried out under an argon atmosphere, unless otherwise noted. All solvents were purified by reported methods.[53] THF was purified by distillation from sodium diphenylketyl before use. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908 instrument with JAI gel 1H+2H columns (Japan Analytical Industry) using chloroform or toluene as eluent. Dry column chromatography (DCC) was carried out with ICN silica DCC 60 A (SiO_2). Preparative thin-layer chromatography (PTLC) and flash column chromatography (FCC) were performed with Merck Kieselgel 60 PF254 (Art. No. 7747) and Merck Silica Gel 60, respectively. The ^{1}H NMR (500 or 300 MHz) and ^{13}C NMR (125 or 75 MHz) spectra were measured in $CDCl_3$, C_6D_6, or $C_2D_2Cl_4$ with a Bruker AM-500, JEOL α-500, or JEOL AL-300 spectrometer using $CHCl_3$ ($\delta = 7.25$ ppm), C_6HD_5 ($\delta = 7.15$ ppm), or C_2HDCl_4 ($\delta = 5.94$ ppm) as internal standards for ^{1}H NMR spectroscopy, and $CDCl_3$ ($\delta = 77.0$ ppm), C_6D_6 ($\delta = 128.0$), or $C_2D_2Cl_4$ ($\delta = 75.5$) as those for ^{13}C NMR spectroscopy. The ^{29}Si NMR (99, 59, or 53 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL α-500 or a JEOL EX-270 spectrometer using tetramethylsilane as an external standard. High-resolution mass spectral data were obtained on a JEOL SX-102 mass spectrometer. The electronic spectra were recorded on a JASCO Ubest-50 UV/Vis or JASCO V-530 UV/Vis spectrometer. Infrared spectra were obtained on a JASCO FT/IR-300E spectrophotometer. Raman spectra were measured at room temperature on a Raman spectrometer consisting of a Spex 1877 Triplemate and an EG&G PARC1421 intensified photodiode array detector. An NEC GLG 108 He–Ne laser (632.8 nm) was used for Raman excitation. All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Reaction of 1 with *tert*-butyl isocyanide (3a): A C_6D_6 (0.5 mL) solution of (*Z*)-1,2-dimesityl-1,2-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}disilene **1**[30] (39 mg, 0.028 mmol) and *tert*-butyl isocyanide (**3a**) (0.02 mL, 0.18 mmol) was placed in a dry 5ϕ NMR tube. After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The mixture was heated at 70°C for 2 h, during which time the reaction was monitored by ^{1}H NMR spectroscopy and the formation of isobutene ($\delta_H = 1.59$ (t, $J = 1$ Hz, 6H), 4.72 (sept, $J = 1$ Hz, 2H)) was observed. After removal of the solvent, the residue was chromatographed (GPLC) to afford (cyano){2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}(mesityl)silane (**4**) (33 mg, 81%). **4**: colorless crystals, M.p. 198–200°C, ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -0.07$ (s, 9H), −0.02 (s, 9H), 0.01 (s, 9H), 0.03 (s, 9H), 0.043 (s, 9H), 0.045 (s, 9H), 1.34 (s, 1H), 2.09 (s, 1H), 2.26 (s, 3H), 2.27 (s, 1H), 2.49 (s, 6H), 5.44 (s, 1H), 6.28 (s, 1H), 6.42 (s, 1H), 6.85 ppm (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 0.5 (q), 0.7 (q), 0.76 (q), 0.80 (q), 0.9 (q), 1.2 (q), 21.1 (q), 24.7 (q), 28.7 (d), 29.0 (d), 30.9 (d), 117.5 (s), 122.9 (d), 125.6 (s), 127.1 (d), 127.7 (d), 129.4 (d), 141.2 (s), 144.3 (s), 146.6 (s), 152.6 (s), 152.8 ppm (s); elemental analysis calcd (%) for $C_{37}H_{71}Si_7 \cdot 0.5\,H_2O$: C 60.42, H 9.87, N 1.90; found: C 60.36, H 9.58, N 2.23.

Reaction of 1 with mesityl isocyanide (3b): A THF (2 mL) suspension of **1** (165 mg, 0.12 mmol) and mesityl isocyanide (**3b**) (34 mg, 0.23 mmol) was placed in a dry Pyrex 12ϕ glass tube. After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The mixture was heated at 70°C for 10 h. After removal of the solvent, the residue was chromatographed (GPLC) to afford 3-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-mesityl-3,5,7-trimethyl-3-sila-3*H*-benzopyrrole (**6b**) (111 mg, 55%). **6b**: colorless crystals, M.p. 224–226°C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -0.15$ (s, 9H), −0.12 (s, 9H), −0.10 (s, 9H), −0.04 (s, 9H), 0.051 (s, 9H), 0.054 (s, 9H), 0.82 (s, 3H), 1.31 (s, 1H), 1.96 (s, 1H), 2.09 (s, 1H), 2.24 (s, 3H), 2.31 (s, 3H), 2.36 (s, 6H), 2.56 (s, 3H), 6.20 (s, 1H), 6.36 (s, 1H), 6.82 (s, 2H), 7.07 (s, 1H), 7.16 ppm (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 0.9$ (q), 1.0 (q), 1.27 (q),1.31 (q), 1.5 (q), 8.6 (q), 17.9 (q), 20.9 (q), 21.3 (q), 24.1 (q), 28.2 (d), 28.4 (d), 30.4 (d), 121.9 (s), 123.1 (d), 128.6 (d), 130.0 (d), 130.8 (d), 132.9 (d), 133.3 (s), 133.7 (s), 136.5 (s), 137.0 (s), 137.3 (s), 138.1 (s), 145.1 (s), 153.1 (s), 153.5 (s), 153.6 (s), 188.9 ppm (s); ^{29}Si NMR (53.5 MHz, $CDCl_3$): $\delta = -9.30$, 1.89, 1.96, 2.02, 2.26, 2.50 ppm; high-resolution FAB-MS: *m*/*z*: 844.4899 ($[M+H]^+$); calcd for $C_{46}H_{82}NSi_7$: 844.4833; elemental analysis calcd (%) for $C_{46}H_{81}NSi_7 \cdot 0.5\,H_2O$: C 64.71, H 9.68, N 1.64; found: C 64.83, H 9.84, N 1.97.

Synthesis of 2,4,6-tris[bis(trimethylsilyl)methyl]phenylformamide (7): A mixture of formic acid (2.5 mL, 65.6 mmol) and acetic anhydride (5.0 mL, 53.0 mmol) was heated at 50°C for 2 h in the air, and 2,4,6-tris[bis(trimethylsilyl)methyl]aniline[22] (905 mg, 1.59 mmol) was added to the mixture. The resulting white suspension was stirred at room temperature for one day, and the reaction mixture was poured into water. After filtration, the precipitates were washed with water and dissolved in $CHCl_3$. The $CHCl_3$ solution was dried with $MgSO_4$ and the solvent was evaporated to give a pure formamide **7** (913 mg, 1.53 mmol, 96%). **7**: white crystals; m.p. 279–280°C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.01$ (s, 36H), 0.04 (s, 18H), 1.37 (s, 1H), 1.84 (s, 1H), 1.91 (s, 1H), 6.25 (d, 1H, $^{3}J = 12$ Hz), 6.37 (s, 1H), 6.50 (s, 1H), 7.80 ppm (d, 1H, $^{3}J = 12$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 0.5$ (q), 0.6 (q), 23.2 (d × 2), 30.4 (d), 121.9 (d), 126.0 (s), 126.7 (d), 143.0 (s × 2), 143.5 (s), 166.2 ppm (d); elemental analysis calcd (%) for $C_{28}H_{61}NOSi_6$: C 56.40, H 10.31, N 2.35; found: C 56.23, H 10.01, N 2.26.

Synthesis of 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl isocyanide (3d): Phosphorus oxychloride (0.02 mL, 0.218 mmol) was added to a CH_2Cl_2 solution (1 mL) of TbtNHCHO (101 mg, 0.169 mmol) and diisopropylamine (0.07 mL, 0.534 mmol) at 0°C. The reaction mixture was stirred at room temperature for 9 h, and an aqueous solution of Na_2CO_3 (ca. 2 mL, 17%) was added to the solution. After stirring for 1 h, the mixture was extracted with $CHCl_3$ and the organic layer was washed with water. The solution was dried with $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was separated by DCC (SiO_2/hexane:CH_2Cl_2 = 5:1) to afford isocyanide **3d** (61.7 mg, 0.107 mmol, 63%) together with the starting material (27.4 mg, 0.046 mmol, 27%). **3d**: white crystals; m.p. 153–155°C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.03$ (s, 18H), 0.04 (s, 36H), 1.37 (s, 1H), 2.07 (s, 1H), 2.13 (s, 1H), 6.34 (s, 1H), 6.46 ppm (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 0.2$ (q), 0.3 (q), 0.5 (q), 25.1 (d × 2), 31.0 (d), 121.1 (d), 121.4 (d), 125.7 (s), 141.3 (s × 2), 144.2 (s), 165.9 ppm (s); elemental analysis calcd (%) for $C_{28}H_{59}NSi_6$: C 58.15, H 10.28, N 2.42; found: C 58.16, H 10.04, N 2.40.

Synthesis of mesityl{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}silylene(*Si*-*C*$^{\alpha}$)2,4,6-triisopropylphenyl isocyanide (5c): An orange suspension of **1** (49.2 mg, 0.0352 mmol) and 2,4,6-triisopropylphenyl isocyanide (**3c**)[32] (16.2 mg, 0.0706 mmol) in C_6D_6 (0.6 mL) was placed in a 5ϕ NMR tube. After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The mixture was heated at 60°C for 2 h to afford the bluish green solution of the corresponding silylene–isocyanide complex **5c**. The molar absorptivity (ε) in the UV/Vis spectrum was calculated by assuming the quantitative generation of **5c**. **5c**: bluish green powder; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 0.19$ (s, 18H), 0.20 (s, 36H), 1,10 (d, 6H, $^{3}J = 7$ Hz), 1.16 (d, 12H, $^{3}J = 7$ Hz), 1,49 (s, 1H), 2.11 (s, 3H), 2.66 (sept, 1H, $^{3}J =$ 7 Hz), 2.73 (s, 1H), 2.80 (s, 6H), 2.84 (s, 1H), 3.59 (sept, 2H, $^{3}J = 7$ Hz), 6.56

(s, 1H), 6.69 (s, 1H), 6.85 (s, 2H), 7.01 ppm (s, 2H); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 1.1$ (q), 1.2 (q), 1.5 (q), 21.1 (q), 23.6 (q), 24.0 (q), 27.5 (q), 29.1 (d), 30.7 (d), 32.9 (d), 33.3 (d), 34.6 (d), 121.9 (d), 122.5 (d), 127.5 (d), 128.6 (d), 129.2 (s), 129.9 (s), 134.0 (s), 138.5 (s), 143.4 (s), 143.6 (s), 145.5(s), 149.4(s), 151.6 (s), 151.7 (s), 209.2 ppm (s); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -53.6$, 1.9, 2.4 ppm ($^1J_{C,Si} = 38.6$ Hz (*Si*CN)); ^{29}Si NMR (99 MHz, THF): $\delta = -55.7$, 1.5, 1.9 ppm; UV/Vis (THF): λ_{max} (ε) = 596 nm (400).

Synthesis of mesityl{2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl}silylene-(*Si-C*$^\alpha$)2,4,6-tris[bis(trimethylsilyl)methyl]phenyl isocyanide (5d): An orange suspension of disilene **1** (49.8 mg, 0.0356 mmol) and the Tbt-substituted isocyanide **3d** (40.0 mg, 0.0692 mmol) in C_6D_6 (0.6 mL) was placed in a 5ϕ NMR tube. After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The mixture was heated at 55 °C for 4 h to afford the greenish blue solution of the corresponding silylene – isocyanide complex **5d**. The molar absorptivity (ε) in the UV/Vis spectrum was calculated by assuming the quantitative generation of **5d**. **5d**: greenish blue powder; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 0.12$ (s, 18H), 0.13 (s, 18H), 0.16 (s, 18H), 0.18 (s, 18H), 0.23 (s, 18H), 0.25 (s, 18H), 1.44 (s, 1H), 1,49 (s, 1H), 2.15 (s, 3H), 2.32 (s, 1H), 2.38 (s, 1H), 2.72 (s, 6H), 3.25 (brs, 2H), 6.54 (s, 1H), 6.60 (s, 1H), 6.66 (s, 1H), 6.73 (s, 1H), 6.82 ppm (s, 2H); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 0.78$ (q), 0.82 (q), 1.0 (q), 1.2 (q), 1.6 (q), 1.9 (q), 21.1 (q), 23.4 (d), 23.8 (d), 28.5 (q), 30.9 (d), 31.2 (d), 32.4 (br d × 2), 122.6 (d), 122.8 (d), 126.4 (s), 127.4 (d), 128.0 (d), 128.3 (s), 129.1 (d), 135.6 (s), 137.5 (s), 140.8 (s), 140.9 (s), 143.8 (s), 144.21 (s), 144.25 (s), 153.6 (s × 2), 196.6 ppm (s); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -57.4$, 1.9, 2.1, 2.3, 3.0 ppm ($^1J_{C,Si} = 22.1$ Hz (*Si*CN)); ^{29}Si NMR (99 MHz, THF): $\delta = -57.9$ ppm (the peaks of TMS region could not be assigned); UV/Vis (THF): λ_{max} (ε) = 397 (3000), 632 nm (100).

Synthesis of mesityl{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}silylene-(*Si-C*$^\alpha$)2,4,6-tri-*tert*-butylphenyl isocyanide (5e): an orange suspension of disilene **1** (52.7 mg, 0.0377 mmol) and 2,4,6-tri-*tert*-butylphenyl isocyanide (**3c**)[37, 54, 55] (20.3 mg, 0.0748 mmol) in C_6D_6 (0.6 mL) was placed in a 5ϕ NMR tube. After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The mixture was heated at 55 °C for 5 h to afford the deep blue solution of the corresponding silylene – isocyanide complex **5e**. The molar absorptivity (ε) in the UV/Vis spectrum was calculated by assuming the quantitative generation of **5e**. **5e**: deep blue powder; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 0.23$ (s, 18H), 0.25 (s, 36H), 1.15 (s, 9H), 1.37 (s, 18H), 1.51 (s, 1H), 2.13 (s, 3H), 2.31 (s, 1H), 2.44 (s, 1H), 2.76 (s, 6H), 6.56 (s, 1H), 6.68 (s, 1H), 6.84 (s, 2H), 7.41 ppm (s, 2H); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 1.20$ (q), 1.73 (q), 1.95 (q), 21.2 (q), 28.0 (q), 30.5 (q), 31.0 (d), 31.1 (q), 32.0 (d), 32.3 (d), 35.3 (s), 36.2 (s), 122.5 (d), 122.8 (d), 124.3 (s), 127.8 (d), 128.7 (d), 134.2 (s), 135.9 (s), 137.9 (s), 141.4 (s), 146.4 (s), 147.3 (s), 149.5 (s), 149.9 (s), 152.2 (s), 178.5 ppm (s); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -48.6$, 1.8, 2.3 ppm ($^1J_{C,Si} = 1.0$ Hz (*Si*CN)); ^{29}Si NMR (99 MHz, THF): $\delta = -48.9$, 1.3, 1.7 ppm; UV/Vis (THF): λ_{max} (ε) = 390 (2000), 671 nm (200).

Theoretical calculations: All theoretical calculations were carried out using the Gaussian 98 program with density functional theory at the B3LYP level. The structural optimization was performed at B3LYP/6 – 31G(d) level and the NMR chemical shifts were calculated at GIAO-B3LYP level (6 – 311G(3d) for Si and 6 – 311G(d) for C, N, and H). The vibrational frequency was calculated at the B3LYP/6 – 31G(d) level and scaled by 0.96. Computation time was provided by the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University.

Typical procedure for preparation of 5c – e: A suspension of disilene **1** (0.045 mmol) and isocyanides **3c – e** (0.095 mmol) in THF (1 mL) was placed in a dry Pyrex 10ϕ glass tube. After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The mixture was heated at 60 °C for 2 h for **3c** or for 7 h for **3d** and **3e** to afford the solution of the corresponding silylene – isocyanide complexes **5c – e**. The sealed tube was opened in a glovebox, and the solution was transferred to another dry Pyrex tube or a flask by using THF (ca. 0.5 mL). This solution was used for the following reactions.

Reaction of silylene – isocyanide complexes 5c – e with triethylsilane

Reaction of ***5c***: A THF solution (ca. 1.5 mL) of the silylene – isocyanide complex **5c** prepared from disilene **1** (65.9 mg, 0.0471 mmol) and isocyanide **3c** (23.0 mg, 0.100 mmol) in THF (1 mL) was placed in a dry Pyrex 10ϕ glass tube. Triethylsilane (0.10 mL, 0.629 mmol) was added to this solution at room temperature. After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The bluish green solution was allowed to stand at ambient temperature for 47 days, but no change could be observed in the color of the solution. Heating at 50 °C for 28 h resulted in the disappearance of the bluish green color and the sealed tube was opened. After removal of the solvent under reduced pressure, the residue was chromatographed (GPLC) and separated by PTLC (hexane:CH_2Cl_2 = 10:1 and 2:1) to afford 1,1,1-triethyl-2-mesityl-2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}disilane (**8**)[28] (51.0 mg, 0.0625 mmol, 66 %) together with isocyanide **3c** (9.6 mg, 0.0419 mmol, 42 %).

Reaction of ***5d***: Silylene – isocyanide complex **5d**, prepared from **1** (74.4 mg, 0.0532 mmol) and **3d** (64.3 mg, 0.111 mmol), was allowed to react with triethylsilane (0.10 mL, 0.629 mmol) in THF (2 mL) at room temperature for 17 days operating a procedure similar to that mentioned above. The separation of the reaction mixture with DCC (SiO_2/hexane) afforded disilane **8** (74.4 mg, 0.0912 mmol, 86 %) together with isocyanide **3d** (60.5 mg, 0.105 mmol, 94 %).

Reaction of ***5e***: Silylene – isocyanide complex **5e**, prepared from disilene **1** (73.4 mg, 0.0525 mmol) and **3e** (29.5 mg, 0.109 mmol), was allowed to react with triethylsilane (0.10 mL, 0.629 mmol) in THF (2 mL) at room temperature for 41 h operating the procedure similar to that mentioned above. The separation of the reaction mixture with GPLC and PTLC (hexane:CH_2Cl_2 = 10:1) afforded disilane **8** (59.3 mg, 0.0727 mmol, 69 %) together with isocyanide **3e** (29.0 mg, 0.107 mmol, 98 %).

Isocyanide-exchange reaction

Reaction of ***5e*** *with* ***3d***: A C_6D_6 solution (0.5 mL) of the silylene – isocyanide complex **5e** prepared from disilene **1** (22.0 mg, 15.7 µmol) and **3e** (8.9 mg, 33 µmol) in C_6D_6 (0.5 mL) was added to **3d** (19.1 mg, 33.0 µmol) and placed in a 5ϕ NMR tube at room temperature. The color of the resulting mixture changed from deep blue to greenish blue. After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The ^{1}H and ^{29}Si NMR spectra of this solution showed the formation of another silylene – isocyanide complex **5d** and a free isocyanide **3e**, though the mixture could not be separated. The ratio of the two silylene – isocyanide complexes was 1:5 (**5e**:**5d**) as judged from the ^{1}H NMR spectrum.

Reaction of ***5d*** *with* ***3c***: Compound **5d**, prepared from disilene **1** (22.2 mg, 15.9 µmol), and **3d** (19.0 mg, 32.9 µmol) were allowed to react with **3c** (7.5 mg, 33 µmol) under the same reaction conditions as those described above. The ^{1}H and ^{29}Si NMR spectra of the reaction mixture showed the formation of **5c** and a free isocyanide **3d**, though the mixture could not be separated. The ratio of two silylene – isocyanide complexes was 1:5 (**5d**:**5c**) as judged from the ^{1}H NMR spectrum.

Reaction of ***5e*** *with* ***3b***: Compound **5e**, prepared from disilene **1** (51.8 mg, 37.0 µmol) and **3e** (20.5 mg, 75.5 µmol), was allowed to react with **3b** (12.0 mg, 82.6 µmol) under the same reaction conditions as those described above. The ^{1}H, ^{13}C and ^{29}Si NMR for this mixture showed the formation of **5b** and a free isocyanide **3e** together with the disappearance of complex **5e**. However, NMR spectra of **5b** could not be fully assigned due to its slow decomposition at room temperature. **5b**: ^{1}H NMR (300 MHz, C_6D_6): δ = 6.53 (s), 2.46 (s), 2.34 (s), 2.24 (s), 1.97 ppm (s), other peaks could not be assigned; ^{13}C NMR (75 MHz, C_6D_6): $\delta = 200.1$ ppm (other peaks could not be assigned); ^{29}Si NMR (59 MHz, C_6D_6): $\delta = -69.2$ ppm (the peaks of TMS region could not be assigned); UV/Vis (THF): λ_{max} = 599 nm.

Thermolysis of silylene – isocyanide complexes 5c – e:

Thermolysis of ***5c***: A suspension of disilene **1** (55.3 mg, 0.0395 mmol) and isocyanide **3c** (20.1 mg, 0.0876 mmol) in THF (1 mL) was placed in a dry Pyrex 10ϕ glass tube. After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The mixture was heated at 60 °C for 2 h to afford the bluish green solution of the silylene – isocyanide complex **5c**. The solution was heated at 80 °C for 22 h, during which time the bluish green color disappeared. After removal of the solvent, the residue was chromatographed (GPLC) and separated by PTLC (hexane:CH_2Cl_2 = 2:1) to afford compound 3,5,7-triisopropyl-2-mesityl-3-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-3-sila-3*H*-benzopyrrole (**6c**) (26.8 mg, 0.0289 mmol, 37 %) together with isocyanide **3c** (0.6 mg, 0.0026 mmol, 3 %). **6c**: pale yellow powder; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): $\delta = -0.07$ (s, 18H; *Me*$_3$Si), 0.02 (s, 18H; *Me*$_3$Si), 0.10 (s, 18H; *Me*$_3$Si), 0.63 (d, 3H; $^3J = 7$ Hz; SiCH*Me*$_2$), 0.94 (d, 3H, $^3J = 7$ Hz; SiCH*Me*$_2$), 1.26 (d, 3H, $^3J = 7$ Hz; CH*Me*$_2$), 1.30 (d, 3H, $^3J = 7$ Hz; CH*Me*$_2$), 1.31 (d, 3H, $^3J = 7$ Hz; CH*Me*$_2$), 1.33 (d, 3H, $^3J = 7$ Hz; CH*Me*$_2$), 1.36 (s, 1H; Tbt *p-CH*), 1.79 (sept, 1H, ^3J = 7 Hz; SiC*H*Me$_2$), 2.15 (brs, 2H; Tbt *o-CH*), 2.26 (s, 3H; Mes *p-Me*), 2.41 (s, 6H; Mes *o-Me*), 2.93 (sept, 1H, $^3J = 7$ Hz; C*H*Me$_2$), 4.06 (sept, 1 H;$^3J = 7$ Hz; C*H*Me$_2$), 6.40 (s, 2 H; Tbt), 6.80 (s, 2 H; Mes), 7.24 (s, 1 H), 7.41 ppm (s, 1 H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 100 °C): $\delta = 2.6$ (q; Si*Me*$_3$), 3.4 (q; Si*Me*$_3$), 3.5 (q; Si*Me*$_3$), 17.3 (d; Si*C*HMe$_2$), 20.7 (q; SiCH*Me*$_2$), 22.20 (q; SiCH*Me*$_2$), 22.25 (q; Mes *p-Me*), 24.9 (q; CH*Me*$_2$), 25.1 (q; CH*Me*$_2$), 25.6 (q; CH*Me*$_2$), 26.1 (q; CH*Me*$_2$), 26.9 (q; Mes *o-Me*), 29.4 (d; *C*HMe$_2$), 29.6 (d; Tbt *o-C*H), 32.3 (d; Tbt *p-C*H), 35.8 (d; *C*HMe$_2$), 126.7 (s), 127.2 (d; Tip), 130.9 (s), 131.0 (d; Tip), 132.0 (d × 2; Mes + Tbt), 138.7 (s), 140.0 (s), 140.4 (s), 145.7 (s), 146.0 (s), 148.5 (s), 154.8 (s), 155.2 (s), 186.7 ppm (s); ^{29}Si NMR (99 MHz, C_6D_6): $\delta = 0.2$, 2.0 ppm; high-resolution FAB-MS: *m*/*z*: 928.5825; calcd for $C_{52}H_{94}NSi_7$: 928.5771.

Thermolysis of ***5d***: A solution of **5d** in THF (1 mL), prepared from disilene **1** (54.7 mg, 0.0390 mmol) and isocyanide **3d** (48.5 mg, 0.0839 mmol), was heated at 80 °C for two days and then at 100 °C for two days operating the procedure similar to that mentioned above. The separation of the reaction mixture with GPLC and DCC (SiO_2/hexane) afforded 4,6-bis[bis(trimethylsilyl)methyl]-1-mesityl-2,2-bis(trimethylsilyl)benzo-1-silacyclobutene (**9**)[28] (35.8 mg, 0.0512 mmol, 65 %) together with isocyanide **3d** (41.3 mg, 0.0714 mmol, 85 %).

Thermolysis of ***5e***: A solution of **5e** in THF (1 mL), prepared from disilene **1** (61.5 mg, 0.0440 mmol) and isocyanide **3e** (25.6 mg, 0.0943 mmol), was heated at 80 °C for two days and then at 100 °C for 9 h operating the procedure similar to that mentioned above. The separation of the reaction mixture with DCC (SiO_2/hexane) afforded **9** (48.1 mg, 0.0688 mmol, 78 %) together with isocyanide **3e** (24.1 mg, 0.0888 mmol, 94 %).

Reaction of silylene – isocyanide complexes 5c – e with 2,3-dimethyl-1,3-butadiene

Reaction of ***5c***: A solution of the silylene – isocyanide complex **5c** in THF (ca. 1.5 mL), prepared from disilene **1** (63.9 mg, 0.0457 mmol) and isocyanide **3c** (22.0 mg, 0.0959 mmol) in THF (1 mL), was placed in a dry Pyrex 10*ϕ* glass tube, and 2,3-dimethyl-1,3-butadiene (0.10 mL, 0.884 mmol) was added at room temperature. After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The bluish green solution was allowed to stand at ambient temperature for five days, but no change could be observed in the color of the solution. Heating at 50 °C for 97 h resulted in the disappearance of the bluish green color and the sealed tube was opened. After removal of the solvent under reduced pressure, the residue was chromatographed (GPLC) and separated by PTLC (hexane:$CH_2Cl_2 = 20{:}1$) to afford 2,5-dihydro-1-mesityl-3,4-dimethyl-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}silole (**10**)[28] (35.0 mg, 0.0448 mmol, 49 %) and 1-(mesityl{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}hydroxysilyl)-2,3-dimethylbut-2-ene (**11**)[28] (10.9 mg, 0.0136 mmol, 15 %) together with isocyanide **3c** (12.8 mg, 0.0558 mmol, 58 %).

Reaction of ***5d***: The silylene – isocyanide complex **5d**, prepared from disilene **1** (62.5 mg, 0.0447 mmol) and isocyanide **3d** (54.8 mg, 0.0948 mmol), was allowed to react with 2,3-dimethyl-1,3-butadiene (0.10 mL, 0.884 mmol) in THF (ca. 1.5 mL) at room temperature for 106 h operating a procedure similar to that described above. The reaction mixture was separated by PTLC (hexane:$CH_2Cl_2 = 10{:}1$) to afford **10** (23.2 mg, 0.0297 mmol, 33 %) and **11** (28.1 mg, 0.0351 mmol, 39 %) together with isocyanide **3d** (50.2 mg, 0.0868 mmol, 92 %).

Reaction of ***5e***: The silylene – isocyanide complex **5e**, prepared from disilene **1** (63.1 mg, 0.0451 mmol) and isocyanide **3e** (25.8 mg, 0.0950 mmol), was allowed to react with 2,3-dimethyl-1,3-butadiene (0.10 mL, 0.884 mmol) in THF (ca. 1.5 mL) at room temperature for 71 h operating a procedure similar to that described above. The reaction mixture was separated by PTLC (hexane:$CH_2Cl_2 = 10{:}1$) to afford **10** (23.7 mg, 0.0303 mmol, 34 %) and **11** (34.1 mg, 0.0426 mmol, 47 %) together with quantitative recovery of isocyanide **3e**.

Observation of an intermediate in the reaction of 5e with 2,3-dimethyl-1,3-butadiene: A solution of the silylene – isocyanide complex **5e** in C_6D_6 (ca. 1.0 mL), prepared from disilene **1** (50.8 mg, 0.0363 mmol) and isocyanide **3e** (21.8 mg, 0.0803 mmol) in C_6D_6 (0.7 mL), was placed in a 5*ϕ* NMR tube, and 2,3-dimethyl-1,3-butadiene (0.10 mL, 0.884 mmol) was added at room temperature. After three freeze-pump-thaw cycles, the tube was evacuated and sealed. After standing at room temperature for 30 min, the ^{1}H, ^{13}C, and ^{29}Si NMR spectra were observed at 25 °C over 2 h, during which time the signals for **5e** almost disappeared. The ^{29}Si NMR spectrum showed three peaks ($\delta = -76.3$, -72.9, and -5.3 ppm with the peak height ratio of approximately 2:6:3) besides the peaks for trimethylsilyl groups. The peak at $\delta = -5.3$ ppm was assigned to **11**, and those at $\delta = -76.3$, and -72.9 ppm were assigned to the geometric isomers of 2-isopropenyl-1-mesityl-2-methyl-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}silacyclopropane (**12**). After standing at room temperature for a further 18 h, the mixture was heated at 50 °C for 7 h. However, no change was observed by NMR spectroscopy. The mixture was heated at 60 °C for 4 h, at 80 °C for 2 h, and 100 °C for 5 h, during which time the reaction was monitored by NMR spectroscopy, and the peaks due to **12** disappeared. After further heating at 100 °C for 6.5 h, the sealed tube was opened and the solvent was evaporated. The residue was separated by PTLC (hexane) to afford **10** (34.3 mg, 0.0439 mmol, 60 %) together with isocyanide **3e** (17.3 mg, 0.0637 mmol, 79 %).

Reaction of 5e with isoprene: Isoprene (0.08 mL, 0.8 mmol) was added at room temperature to a solution of the silylene – isocyanide complex **5e** in THF (ca. 1.5 mL), prepared from disilene **1** (56.1 mg, 0.040 mmol) and isocyanide **3e** (23.9 mg, 0.088 mmol) in THF (1 mL). Stirring of the deep blue solution for 10 min at ambient temperature resulted in the disappearance of the color. After further stirring for 2.5 h, the mixture was separated by GPLC (solvent: toluene) to afford **13** (51.7 mg, 0.0673 mmol, 84 %) together with isocyanide **3e** (23.2 mg, 0.0855 mmol, 97 %). **13**: colorless powder, m.p. 172 – 175 °C (decomp); ^{1}H NMR (500 MHz, C_6D_6, 75 °C): $\delta = 0.01$ (s, 18 H), 0.14 (s, 9 H), 0.15 (s, 9 H), 0.28 (s, 18 H), 1.41 – 1.49 (m, 3 H), 1.86 (s, 3 H), 2.04 (s, 3 H), 2.44 – 2.47 (m, 1 H), 2.67 (s, 6 H), 2.89 (br s, 2 H), 4.32 (s, 1 H), 4.43 (s, 1 H), 6.57 (s, 2 H), 6.70 ppm (s, 2 H); ^{13}C NMR (125 MHz, C_6D_6, 75 °C): $\delta = 1.0$ (q), 1.2 (q), 2.1 (q), 11.9 (t), 21.0 (q), 25.0 (q), 26.5 (q), 29.3 (d), 29.9 (d), 31.3 (d), 103.7 (t), 125.8 (s), 128.3 (d), 128.6 (s), 128.7 (d), 139.6 (s), 145.4 (s), 145.6 (s), 145.7 (s), 153.5 ppm (s); ^{29}Si NMR (99 MHz, C_6D_6, 75 °C): $\delta = -88.5$, 2.6 ppm; elemental analysis calcd (%) for $C_{41}H_{78}Si_7 \cdot H_2O$: C 62.68, H 10.26; found: C 62.59, H 10.07.

Thermolysis of 13: A C_6D_6 solution of **13** (25.2 mg, 0.0328 mmol) was heated at 160 °C for 14 days in a sealed tube. The mixture was purified with PTLC (hexane:$CH_2Cl_2 = 20{:}1$) to give 2,5-dihydro-1-mesityl-3-methyl-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}silole (**14**) (22.1 mg, 0.0288 mmol, 88 %). **14**: colorless powder, m.p. 159 – 161 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -0.09$ (s, 9 H), -0.08 (s, 9 H), -0.02 (s, 9 H), -0.01 (s, 9 H), 0.04 (s, 18 H), 1.28 (s, 1 H), 1.78 (s, 3 H), 1.78 – 1.84 (m, 1 H; C*H*$_2$CH), 1.88 (d, 1 H, $^2J = 19$ Hz; C*H*$_2$CMe), 2.02 (d, 1 H, $^2J = 19$ Hz; C*H*$_2$CMe), 2.06 (s, 1 H), 2.09 – 2.15 (m, 1 H; C*H*$_2$CH), 2.16 (s, 1 H), 2.21 (s, 3 H), 2.37 (s, 6 H), 5.56 (m, 1 H), 6.24 (s, 1 H), 6.37 (s, 1 H), 6.74 ppm (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 0.89$ (q), 0.93 (q), 1.1 (q), 1.2 (q), 1.4 (q), 1.5 (q), 20.8 (q), 22.4 (q), 25.6 (q), 26.0 (t), 27.6 (d), 27.9 (d), 29.4 (t), 30.3 (d), 122.8 (d), 125.4 (d), 128.0 (d), 128.9 (s), 129.4 (d), 137.1 (s), 138.2 (s), 140.0 (s), 143.2 (s), 143.5 (s), 151.6 (s),151.8 ppm (s); ^{29}Si NMR (99 MHz, $CDCl_3$): $\delta = 1.7$, 2.2, 2.4, 2.6 ppm; elemental analysis calcd (%) for $C_{41}H_{78}Si_7$: C 64.15, H 10.24; found: C 64.14, H 10.15.

Reaction of silylene – isocyanide complexes 5c – e with methanol

Reaction of ***5c*** *at room temperature*: Methanol (0.07 mL, 1.73 mmol) was added at room temperature to a solution of the silylene – isocyanide complex **5c** in THF (ca. 2.0 mL), prepared from disilene **1** (90.5 mg, 0.0647 mmol) and isocyanide **3c** (32.3 mg, 0.141 mmol) in THF (1.5 mL). Stirring for 5 min resulted in the disappearance of the bluish green color. After stirring for 25 h, the solvent was evaporated. The residue was separated by PTLC (hexane:$CH_2Cl_2 = 10{:}1$) to afford mesityl(methoxy)-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}silane (**15**)[28] (66.1 mg, 0.0964 mmol, 70 %) and methyl 1-mesityl-*N*-(2,4,6-triisopropylphenyl)-1-({2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}silanecarboximidate (**16c**) (9.1 mg, 0.0947 mmol, 7 %) together with isocyanide **3c** (17.4 mg, 0.0759 mmol, 54 %). **16c**: white powder; m.p. 191 – 192 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -0.069$ (s, 9 H), -0.065 (s, 9 H), -0.06 (s, 9 H), 0.00 (s, 9 H), 0.04 (s, 18 H), 0.67 (s, 3 H), 0.87 (s, 3 H), 1.03 (s, 3 H), 1.20 (d, 3 H, $^3J = 7$ Hz), 1.21 (d, 3 H, $^3J = 7$ Hz), 1.29 (s × 2, 1 H + 3 H), 1.66 (s, 3 H), 1.82 (br s, 1 H), 1.99 (s, 1 H), 2.11 (s, 1 H), 2.17 (s, 3 H), 2.31 (s, 3 H), 2.79 (d, 1 H, $^3J = 7$ Hz), 3.17 (br s, 1 H), 3.69 (s, 3 H), 5.33 (s, 1 H), 6.26 (s, 1 H), 6.38 (s, 1 H), 6.52 (s, 1 H), 6.55 (s, 1 H), 6.65 (s, 1 H), 6.85 ppm (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 0.9$ (q), 0.95 (q), 0.99 (q), 1.27 (q), 1.35 (q), 20.7 (q), 21.0 (q), 21.6 (q), 23.0 (q), 23.3 (q), 23.8 (q), 24.2 (q), 24.5 (q), 25.4 (q), 27.8 (d), 28.0 (d), 28.1 (d), 28.4 (d), 30.4 (d), 34.1 (d), 52.4 (q), 119.5 (d), 119.7 (d), 122.3 (s), 123.0 (d), 128.3 (d), 128.9 (d), 129.4 (d), 129.7 (s), 134.5 (s), 137.8 (s), 139.0 (s), 140.7 (s), 142.1 (s), 144.1 (s × 2), 144.6 (s), 152.3 (s), 152.7 (s), 166.4 ppm (s); ^{29}Si NMR (99 MHz, $CDCl_3$): $\delta = -51.1$, 1.7, 1.8, 2.26, 2.31, 2.4 ppm; IR (KBr): $\tilde{\nu} = 2206$ cm^{-1} (Si–H stretching); high-resolution FAB-MS: *m*/*z*: 959.6489; calcd for $C_{53}H_{97}NOSi_7$: 959.5955; elemental analysis calcd (%) for $C_{53}H_{97}NOSi_7$: C 66.24, H 10.17, N 1.46; found: C 66.07, H 9.96, N 1.39.

*Reaction of **5d** at room temperature*: The silylene – isocyanide complex **5d**, prepared from disilene **1** (63.1 mg, 0.0451 mmol) and isocyanide **3d** (54.1 mg, 0.0936 mmol), was allowed to react with methanol (0.05 mL, 1.23 mmol) in THF (1.5 mL) under the reaction conditions similar to those described above. The reaction mixture was separated by PTLC (hexane:CH_2Cl_2 = 10:1) and GPLC to afford **15** (57.0 mg, 0.0779 mmol, 86%) together with isocyanide **3d** (49.1 mg, 0.0849 mmol, 91%).

*Reaction of **5e** at room temperature*: The silylene – isocyanide complex **5e**, prepared from disilene **1** (63.2 mg, 0.0452 mmol) and isocyanide **3e** (25.5 mg, 0.0939 mmol), was allowed to react with methanol (0.05 mL, 1.23 mmol) in THF (1.5 mL) under the reaction conditions similar to those described above. The reaction mixture was separated by PTLC (hexane:CH_2Cl_2 = 10:1) to afford **15** (49.4 mg, 0.0675 mmol, 75%) together with isocyanide **3e** (25.1 mg, 0.0925 mmol, 98%).

*Reaction of **5c** at low temperature*: Methanol (0.05 mL, 1.23 mmol) was added to a THF solution (ca. 1.5 mL) of the silylene – isocyanide complex **5c** prepared from disilene **1** (66.7 mg, 0.0477 mmol) and isocyanide **3c** (25.3 mg, 0.110 mmol) in THF (1 mL) at − 78 °C. The resulting bluish green solution was warmed to 0 °C over 4.5 h, during which time the bluish green color disappeared. After removal of the solvent under reduced pressure, the residue was chromatographed (GPLC) and separated by PTLC (hexane:CH_2Cl_2 = 20:1) to afford **15** (6.6 mg, 0.0092 mmol, 10%) and **16c** (36.4 mg, 0.0379 mmol, 40%) together with isocyanide **3c** (5.1 mg, 0.0222 mmol, 20%).

*Reaction of **5d** at low temperature*: Methanol (0.05 mL, 1.23 mmol) was added to a solution of the silylene – isocyanide complex **5d** in THF (ca. 1.5 mL), prepared from disilene **1** (56.2 mg, 0.0402 mmol) and isocyanide **3d** (51.9 mg, 0.0897 mmol) in THF (1 mL), at − 78 °C. The resulting greenish blue solution was warmed to 7 °C over 5.5 h, during which time the greenish blue color disappeared. After removal of the solvent under reduced pressure, the residue was separated by DCC (SiO_2/hexane:CH_2Cl_2 = 10:1) to afford **5d** (45.9 mg, 0.0627 mmol, 78%) together with isocyanide **3d** (48.8 mg, 0.0844 mmol, 94%).

Monitoring of the reaction of 5e with sodium methoxide by ^{29}Si NMR spectroscopy: A THF suspension (ca. 1 mL) of sodium methoxide (20.9 mg, 0.387 mmol) and the silylene – isocyanide complex **5c** prepared from disilene **1** (54.0 mg, 0.0386 mmol) and isocyanide **3e** (23.4 mg, 0.0862 mmol) in THF (0.5 mL) was placed in a 5ϕ NMR tube with a sealed capillary, to which C_6D_6 was introduced. After five freeze-pump-thaw cycles, the tube was evacuated and sealed. When the mixture was allowed to stand at ambient temperature for 6 h, no change was observed in the ^{29}Si NMR spectrum of the mixture.

Reaction of sylilene-isocyanide complexes 5c – e with hydrogen chloride

*Reaction of **5c***: An solution of HCl (1.0 M, 0.5 mL, 0.5 mmol) in diethyl ether was added to a solution of the silylene – isocyanide complex **5c** in THF (ca. 1.5 mL), prepared from disilene **1** (60.0 mg, 0.0429 mmol) and isocyanide **3c** (21.6 mg, 0.0942 mmol) in THF (1 mL) at − 78 °C. A saturated aqueous solution of $NaHCO_3$ was added to the resulting orange solution at − 78 °C, and the mixture was warmed to room temperature. The mixture was extracted with $CHCl_3$, and the organic layer dried with $MgSO_4$. After removal of the solvent under reduced pressure, the residue was chromatographed (GPLC) and separated by PTLC (hexane:CH_2Cl_2 = 10:1 and 5:1) to afford chloro(mesityl){2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl}silane (**18**) (25.6 mg, 0.0348 mmol, 41%) together with **3c** (9.2 mg, 0.0401 mmol, 43%). **18**: white powder; m.p. 191 – 193 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = − 0.09 (s, 9H), − 0.07 (s, 9H), − 0.01 (s, 9H), 0.02 (s, 9H), 0.04 (s, 18H), 1.33 (s, 1H), 2.25 (s, 3H), 2.26 (s, 1H), 2.40 (s, 1H), 2.47 (s, 6H), 5.93 (s, 1H), 6.26 (s, 1H), 6.39 (s, 1H), 6.83 ppm (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.8 (q), 0.9 (q), 1.1 (q), 1.2 (q), 21.1 (q), 25.0 (q), 27.4 (d), 27.6 (d), 30.8 (d), 122.7 (d), 123.1 (s), 127.6 (d), 129.6 (d), 129.9 (s), 140,5 (s), 144.0 (s), 146.1 (s), 152.5 (s), 152.8 ppm (s); elemental analysis calcd (%) for $C_{36}H_{71}ClSi_7$: C 58.75, H 9.72, Cl 4.82; found: C 59.00, H 9.54, Cl 4.61.

*Reaction of **5d***: A solution of HCl (1.0 M, 0.5 mL, 0.5 mmol) in diethyl ether was added to a solution of the silylene – isocyanide complex **5d** in THF (ca. 1.5 mL), prepared from disilene **1** (54.4 mg, 0.0389 mmol) and isocyanide **3d** (49.8 mg, 0.0861 mmol) in THF (1 mL) at − 78 °C. The resulting yellow solution was warmed to room temperature, and the solvent was evaporated. The residue was chromatographed (GPLC) and separated by DCC (SiO_2/hexane:CH_2Cl_2 = 20:1) to afford **18** (43.1 mg, 0.0586 mmol, 75%) together with **3d** (46.0 mg, 0.0795 mmol, 92%).

*Reaction of **5e***: A solution of HCl (1.0 M, 0.5 mL, 0.5 mmol) in diethyl ether was added to a solution of the silylene – isocyanide complex **5e** in THF (ca. 1.5 mL) prepared from disilene **1** (57.8 mg, 0.0413 mmol) and isocyanide **3e** (24.7 mg, 0.0910 mmol) in THF (1 mL) at − 78 °C. The resulting yellow solution was warmed to room temperature, and the solvent was evaporated. The residue was chromatographed (GPLC) and separated by PTLC (hexane:CH_2Cl_2 = 10:1) to afford **18** (45.8 mg, 0.0622 mmol, 75%) together with **3e** (21.5 mg, 0.0818 mmol, 90%).

Reaction of sylilene-iosocyanide complexes 5c – e with methyl iodide

*Reaction of **5c***: Methyl iodide (0.05 mL, 0.803 mmol) was added to a solution of the silylene – isocyanide complex **5c** in THF (ca. 1.5 mL), prepared from disilene **1** (61.7 mg, 0.0441 mmol) and isocyanide **3c** (24.6 mg, 0.107 mmol) in THF (1 mL) at − 78 °C. The resulting bluish green solution was warmed to − 40 °C over 30 min, during which time the bluish green color disappeared. The mixture was warmed to room temperature, and the solvent was evaporated. The residue was chromatographed (GPLC) and separated by PTLC (hexane:CH_2Cl_2 = 10:1) to afford iodo(mesityl)(methyl){2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}silane (**19**) (11.9 mg, 0.0141 mmol, 16%), and mesityl(methyl){2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}hydroxysilane (**20**) (13.1 mg, 0.0179 mmol, 20%) together with **3c** (6.8 mg, 0.0296 mmol, 28%). **19**: white powder; m.p. 215 – 217 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = − 0.14 (s, 9H), − 0.08 (s, 9H), 0.040 (s, 9H), 0.044 (s, 9H), 0.08 (s, 9H), 0.12 (s, 9H), 1.29 (s, 1H), 1.68 (s, 3H), 2.24 (s × 2, 3H + 1H), 2.45 (s × 2, 6H + 1H), 6.24 (s, 1H), 6.38 (s, 1H), 6.75 ppm (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.8 (q), 1.0 (q), 1.1 (q), 1.4 (q), 1.8 (q), 2.1 (q), 17.5 (q), 20.9 (q), 25.9 (q), 27.5 (d), 27.7 (d), 30.5 (d), 123.3 (s), 123.5 (d), 128.6 (d), 130.0 (d), 134.8 (s), 139.8 (s), 144.9 (s × 2), 151.0 (s), 151.5 ppm (s); elemental analysis calcd (%) for $C_{37}H_{73}ISi_7$: C 52.81, H 8.74, I 15.08; found: C 52.87, H 8.56, I 15.50; **20**: white powder; m.p. 214 – 215 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = − 0.14 (s, 9H), − 0.08 (s, 9H), 0.02 (s, 9H), 0.03 (s, 27H), 0.76 (s, 3H), 1.30 (s, 1H), 1.88 (s, 1H), 2.21 (s, 3H), 2.27 (s, 1H), 2.39 (s × 2, 6H + 1H), 6.22 (s, 1H), 6.36 (s, 1H), 6.74 ppm (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.7 (q), 0.8 (q), 0.9 (q), 1.1 (q), 1.4 (q), 1.7 (q), 10.3 (q), 20.9 (q), 24.7 (q), 26.8 (d), 27.0 (d), 30.4 (d), 122.9 (d), 128.0 (d), 129.5 (d), 129.6 (s), 135.5 (s), 138.7 (s), 143.0 (s), 144.3 (s), 151.0 (s), 151.2 ppm (s); elemental analysis calcd (%) for $C_{37}H_{74}OSi_7$: C 60.75, H 10.20, found: C 60.96, H 9.98.

*Reaction of **5d***: Methyl iodide (0.05 mL, 0.803 mmol) was added to a solution of the silylene – isocyanide complex **5d** in THF (ca. 1.5 mL), prepared from disilene **1** (58.6 mg, 0.0419 mmol) and isocyanide **3d** (54.1 mg, 0.0936 mmol) in THF (1 mL) at − 78 °C. The resulting greenish blue solution was warmed to room temperature over 2 h, during which time the greenish blue color disappeared. After removal of the solvent, the residue was separated by PTLC (hexane:CH_2Cl_2 = 15:1) to afford **19** (20.7 mg, 0.0246 mmol, 29%) and **20** (10.4 mg, 0.0142 mmol, 17%) together with **3d** (53.2 mg, 0.0920 mmol, 98%).

*Reaction of **5e***: Methyl iodide (0.05 mL, 0.803 mmol) was added to a solution of the silylene – isocyanide complex **5e** in THF (ca. 1.5 mL), prepared from disilene **1** (59.7 mg, 0.0427 mmol) and isocyanide **3e** (25.8 mg, 0.0950 mmol) in THF (1 mL), at − 78 °C. The resulting deep blue solution was warmed to − 20 °C over 1 h, during which time the deep blue color disappeared. The mixture was warmed to room temperature, and the solvent was evaporated. The residue was separated by PTLC (hexane:CH_2Cl_2 = 15:1) to afford **19** (13.9 mg, 0.0165 mmol, 19%), and **20** (11.5 mg, 0.0157 mmol, 18%) together with **3e** (25.1 mg, 0.0925 mmol, 97%).

Trapping of an intermediate in the reaction of 5c with methyl iodide: Methyl iodide (0.05 mL, 0.803 mmol) was added to a solution of the silylene – isocyanide complex **5e** in THF (ca. 1.5 mL), prepared from disilene **1** (56.8 mg, 0.0406 mmol) and isocyanide **3c** (22.7 mg, 0.0990 mmol) in THF (1 mL), at − 78 °C. The resulting bluish green solution was warmed to − 50 °C over 2 h, during which time the bluish green color changed to orange. Methanol (0.05 mL, 1.23 mmol) was added to the resulting orange solution at − 50 °C, and the reaction mixture was warmed to room temperature. After removal of the solvent, the residue was chromatographed (GPLC) and separated by PTLC (hexane:CH_2Cl_2 = 20:1) to afford mesityl(methyl){2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}methoxysilane (**21**) (17.4 mg, 0.0233 mmol, 29%) together with **3e** (8.0 mg, 0.0109 mmol, 13%). **21**: white powder; m.p. 181–183 °C; ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = -0.14$ (s, 9H), −0.11 (s, 9H), −0.02 (s, 9H), 0.00 (s, 9H), 0.03 (s, 18H), 0.75 (s, 3H), 1.27 (s, 1H), 2.22 (s, 3H), 2.35 (s × 2, 6H + 1H), 2.52 (s, 1H), 3.22 (s, 3H) 6.19 (s, 1H), 6.33 (s, 1H), 6.75 ppm (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): $\delta = 0.8$ (q), 1.1 (q), 1.2 (q), 1.4 (q), 1.5 (q), 5.9 (q), 20.9 (q), 25.1 (q), 26.8 (d), 26.9 (d), 30.2 (d), 48.9 (q), 122.8 (d), 127.9 (d), 128.3 (s), 129.5 (d), 133.7 (s), 138.8 (s), 143.8 (s), 144.1 (s), 151.5 (s), 151.8 ppm (s); elemental analysis calcd (%) for $C_{38}H_{76}OSi_7$: C 61.21, H 10.27; found: C 60.73, H 9.79.

Reaction of iodosilane 19 with methanol in the presence of 3c (a control experiment for the trapping by methanol): A solution of iodosilane **19** (36.3 mg, 0.0431 mmol), isocyanide **3c** (20.8 mg, 0.907 mmol), and methanol (0.2 mL, 4.94 mmol) in THF (0.8 mL) was stirred at room temperature for one day. After removal of the solvent, the residue was purified by GPLC. The ^{1}H NMR spectrum showed the formation of a very small amount of **21** (<5%).

Trapping of an intermediate in the reaction of 5e with methyl iodide: Methyl iodide (0.05 mL, 0.803 mmol) was added to a solution of the silylene–isocyanide complex **5e** in THF (ca. 1.5 mL), prepared from disilene **1** (54.1 mg, 0.0387 mmol) and isocyanide **3e** (23.1 mg, 0.0851 mmol) in THF (1 mL) at −78 °C. The resulting deep blue solution was warmed to −20 °C over 3 h, during which time the deep blue color changed to orange. Methanol (0.05 mL, 1.23 mmol) was added to the resulting orange solution at −78 °C, and the reaction mixture was warmed to room temperature. After removal of the solvent, the residue was chromatographed (GPLC) and separated by PTLC (hexane:CH$_2$Cl$_2$ = 20:1) to afford **21** (ca. 11 mg, 0.014 mmol, 18%)[50] and **20** (7.7 mg, 0.0105 mmol, 14%) together with **3e** (20.8 mg, 0.0766 mmol, 90%).

Reaction of iodosilane 19 with methanol in the presence of 3e (a control experiment for trapping by methanol): A solution of iodosilane **19** (18.6 mg, 0.0221 mmol), isocyanide **3e** (21.0 mg, 0.0774 mmol), methyl iodide (0.05 mL, 0.803 mmol), and methanol (0.05 mL, 1.23 mmol) in THF (0.5 mL) was placed in a dry Pyrex 10ϕ glass tube. After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The solution was allowed to stand at ambient temperature for three days and the solvent was evaporated. The ^{1}H NMR spectrum of the residue showed the formation of a very small amount of **21** (<5%).

Observation of an intermediate in the reaction of 5e with methyl iodide: A solution of the silylene–isocyanide complex **5e** in THF (ca. 1 mL), prepared from disilene **1** (46.0 mg, 0.0329 mmol) and isocyanide **3e** (20.0 mg, 0.0737 mmol) in THF (0.5 mL), was placed in a 5ϕ NMR tube with a sealed capillary into which [D$_6$]acetone was introduced. Methyl iodide (0.04 mL, 0.643 mmol) was added to the solution at −78 °C, and the tube was evacuated and sealed, still at −78 °C. The mixture was warmed to −20 °C, during which time **5e** was consumed by reaction with methyl iodide, and the sealed tube was inserted in the NMR probe that was cooled to −50 °C. Signals for the intermediate, 1-mesityl-1-methyl-*N*-(2,4,6-tri-*tert*-butylphenyl)-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}silanecarbonitrilium iodide (**22e**), were observed at −10 °C by ^{29}Si NMR spectroscopy. After the NMR measurements, the solvent was removed under reduced pressure. The residue was chromatographed (GPLC) and separated by PTLC (hexane:CH$_2$Cl$_2$ = 20:1) to afford **19** (23.4 mg, 0.0278 mmol, 42%) together with **3e** (18.8 mg, 0.0693 mmol, 94%). The ^{13}C NMR spectrum of the intermediate **22c** was measured by performing the reaction of the ^{13}C-labeled silylene–isocyanide complex ^{13}C-**5e**, prepared from disilene **1** (47.0 mg, 0.0336 mmol) and ^{13}C-**3e** (19.9 mg, 0.0730 mmol) in THF (0.4 mL), with methyl iodide (0.05 mL, 0.803 mmol) by the same procedure.

X-ray data collection of compounds 3d and 6b: Single crystals of **3d** and **6b** were grown by slow evaporation of a saturated solution in hexane and dichloromethane–methanol, respectively, at room temperature. The intensity data were collected on Rigaku/MSC Mercury CCD diffractometer (for **3d**) or Rigaku AFC7R diffractometer (for **6b**) with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71070$ Å for **3d** and $\lambda = 0.71069$ Å for **6b**). The structures were solved by direct methods (SIR-97)[56] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97).[57] All the non-hydrogen atoms were refined anisotropically. All hydrogens were placed using AFIX instructions. Crystal data for **3d** ($C_{28}H_{59}NSi_6$): $M_r = 578.30$; $T = 103(2)$ K; monoclinic; *Cc* (no.14); $a = 16.030(9)$, $b = 18.907(10)$, $c = 12.445(6)$ Å; $\beta = 99.045(8)°$; $V = 3725(3)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.031$ g cm^{-3}; $\mu = 0.240$ mm^{-1}; $2\theta_{max} = 54.94$; 14494 reflections measured; 7700 independent reflections; 334 refined parameters; GOF = 1.032; $R_1 = 0.0333$ and w$R_2 = 0.0804$ [$I > 2\sigma(I)$]; $R_1 = 0.0352$ and w$R_2 = 0.0815$ [for all data]; largest diff. peak and hole 0.342 and −0.187 e Å^{-3}. Crystal data for **6b** ($C_{46}H_{81}NSi_7$): $M_r = 844.75$; $T = 298(2)$ K; monoclinic; $P2_1/n$ (no.14); $a = 9.762(7)$, $b = 22.700(6)$, $c = 24.767(6)$ Å; $\beta = 93.44(4)°$; $V = 5478(5)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.024$ g cm^{-3}; $\mu = 0.202$ mm^{-1}; $\lambda = 0.71069$ Å; $2\theta_{max} = 50.0$; 8897 reflections measured; 8231 independent reflections; 487 refined parameters; GOF = 0.961; $R_1 = 0.0936$ and w$R_2 = 0.1881$ [$I > 2\sigma(I)$]; $R_1 = 0.2992$ and w$R_2 = 0.2774$ [for all data]; largest diff. peak and hole 0.238 and −0.234 e Å^{-3}.

CCDC-199143 (**3d**) and CCDC-199142 (**6b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallograhic data Centre, 12 Union Road, Cambridge, CB21EZ, UK; fax: (+44)1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk).

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