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Disilenes

The Addition of Nitriles to Tetramesityldisilene: A Comparison of the Reactivity between Surface and Molecular Disilenes

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Dedicated to Prof. Dr. Matthias Driess, Prof. Dr. Martin Oestreich, and Dr. Richard Weidner for their superb organization of the 17th International Symposium on Silicon Chemistry and the 7th European Silicon Days

Abstract: The addition of acetonitrile, propionitrile, and phenylacetonitrile to tetramesityldisilene ($Mes_2Si{=}SiMes_2$) was examined. In general, 1,2,3-azadisiletines and the tautomeric enamines were formed, although a ketenimine was formed as the major product in the addition of phenylacetonitrile to the disilene. In the presence of LiCl, the mode of addition changed for both acetonitrile and propionitrile: insertion into the α-CH bond of acetonitrile and/or formation of the formal HCN adduct was observed. Preliminary investigations of the reactivity of the nitrile adducts are also reported. A comparison between the reactivity of nitriles with $Mes_2Si{=}SiMes_2$ and the Si(100)-2×1 surface was made both in terms of the types of adducts formed and their reactivity. Some insights into the surface chemistry are offered.

Introduction

The attachment of organic molecules to semiconductor surfaces has been extensively investigated over the past two decades.[1] With potential applications in the area of biosensors,[1b] the addition of nitriles to the Si(100)-2×1 surface is of particular interest. If the nitrile group remains intact after reaction with the surface, the nitrile group may be subsequently hydrolyzed to a carboxylic acid or reduced to a terminal amine and biologically active molecules, such as peptides or proteins, could then be bound as a second layer. If, on the other hand, the nitrile moiety reacts directly with the surface, different surface reactivity can be expected demonstrating the need to have a clear understanding of the structure of the organic group present on the surface.

The addition of acetonitrile to the Si(100)-2×1 surface was first reported by Xu in 2001.[2] Since the initial study, the addition of acetonitrile to the Si(100)-2×1 surface has been examined at various temperatures, including room temperature, and the adducts have been identified using a variety of techniques, including temperature-programmed desorption (TPD),[2] high-resolution electron energy loss spectroscopy (HREELS),[2] conventional X-ray photoelectron spectroscopy (XPS),[2,3] synchrotron radiation XPS,[4,5] near-edge X-ray absorption fine structures (NEXAFS),[4,5] resonant Auger electron spectroscopy (RAES),[6] and multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy.[3] Current theoretical[2,5,7–10] and experimental[3,5,6] evidence supports the formation of three types of nitrile adducts in equal amounts on the Si surface at room temperature: an α-CH insertion adduct (**1**), a cycloadduct involving the C≡N bond (**2a**,**b**), and a twisted ketenimine product (**3a**,**b**) (Figure 1). Despite many studies of this reaction, only **1** has been identified unambiguously. The presence of distinct adducts (**2** and **3**) with C=N and C=C=N moieties on the surface have been confirmed; however, only the functional group and the orientation of the π system relative to the Si dimer axis are known. The exact structures of **2** and **3** have not been established due to the limitations of the experimental techniques employed.

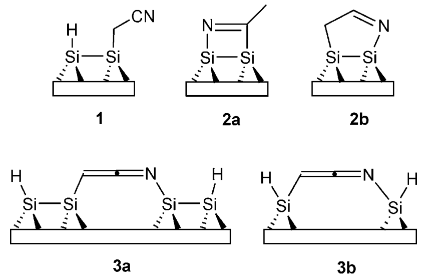

Figure 1. Acetonitrile adducts formed on the Si(100)-2×1 surface

In contrast to surface adducts, the structures of molecular compounds can be identified unambiguously by using experimental techniques that are not available to surface scientists, such as NMR spectroscopy and X-ray crystallography. Additionally, molecular compounds and surface adducts can be characterized by FTIR spectroscopy, which allows for a comparison between the data sets. Furthermore, the reactivity of molecular compounds can be examined more easily than the reactivity of

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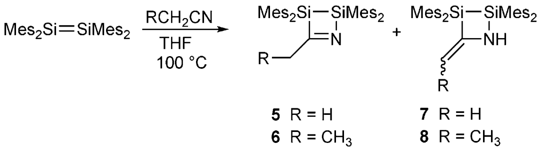
surface adducts, especially when the surface layer contains several reactive functionalities.

$Mes_2Si{=}SiMes_2$ (**4**) is a reasonable model for the Si(100)-2×1 surface,[11] as it has been demonstrated that **4** is comparable in reactivity to the Si surface.[12] For example, disilene **4** and Si(100)-2×1 surface dimers exhibit the same reactivity towards alkynes.[1d,g–k,13,14] Surprisingly, the reactivity of disilenes towards nitriles has not yet been thoroughly examined;[15–18] in fact, there are no reports of the direct addition of acetonitrile, or any nitrile with α-hydrogen atoms on a saturated carbon atom, to disilenes. Herein, we examine the addition of acetonitrile to tetramesityldisilene, **4**, in order to compare the structures of the molecular adducts with the structures of the acetonitrile adducts formed on the Si(100)-2×1 surface and to provide further insight into the structures present on the surface. The reactivity of propionitrile and phenylacetonitrile towards disilene **4** was also studied to investigate reactivity trends.

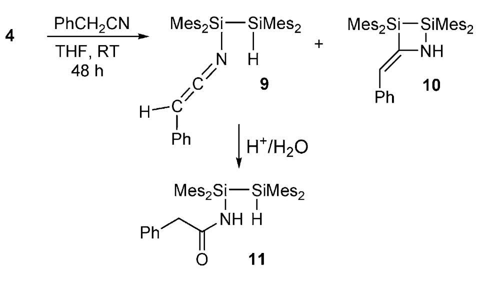
Results and Discussion

No reaction was observed upon the addition of excess CH_3CN (or CH_3CH_2CN) to disilene **4** in THF at room temperature, and thus, the reaction mixtures were heated in a sealed tube to 100 °C. The 1,2,3-azadisiletine **5** (or **6**) was the initially formed product; however, over time and/or upon handling or exposure to the ambient atmosphere, the enamine tautomer, **7** (or **8**), appears to form at the expense of the imine (Scheme 1).

In contrast, the addition of excess $PhCH_2CN$ to disilene **4** in THF at room temperature gave a mixture of **9** and **10** in a ratio of about 5:1 (Scheme 2). Compound **9** hydrolyzed slowly to **11** upon exposure to the ambient atmosphere; however, upon the addition of acid (1/2 drop of 1 M HCl) or upon attempted purification by chromatography, **9** rapidly hydrolyzed to **11**. Compound **10** also decomposed to an unidentified compound under these conditions.

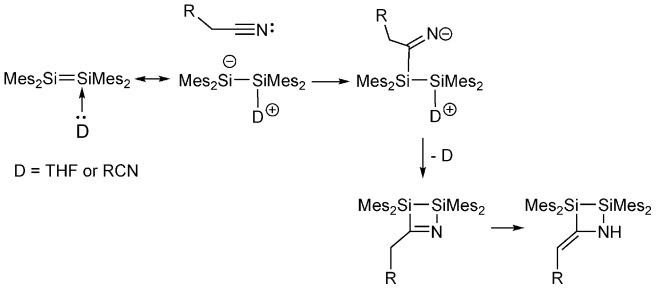


Scheme 1. Addition of CH_3CN and CH_3CH_2CN to disilene **4**



Scheme 2. Addition of $PhCH_2CN$ to disilene **4**

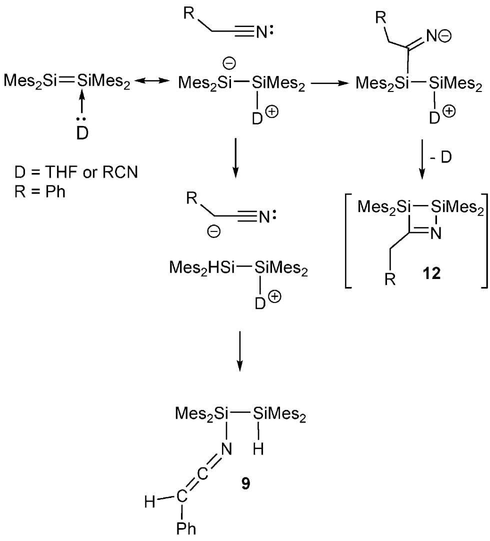
The formation of 1,2,3-azadisiletines **5** and **6** can be understood in terms of a formal [2+2] cycloaddition between the C≡N bond of the nitrile and the Si=Si bond of **4**. Enamines **7** and **8** likely form as a result of tautomerization of the initial 1,2,3-azadisiletines. The addition of aceto- and propionitrile to disilene **4** likely begins with coordination of a donor molecule (D = THF or a molecule of nitrile) to **4** to give a complex (Scheme 3). Although THF or nitrile complexes of **4** have not been observed, water and alcohols are known to coordinate to **4**[19] and a weak interaction between a donor molecule and **4** may be sufficient to polarize the Si=Si bond. Furthermore, complexation between the nitrilic nitrogen of acrylonitrile and the silicon dimer on the Si(100)-2×1 surface has been proposed to occur,[20] and adducts between stronger donors such as NHCs or isonitriles have recently been reported.[21] After coordination of the donor molecule to the disilene, the basic portion of the complex may attack the nitrilic carbon to give a zwitterionic intermediate. The intermediate may then undergo intramolecular nucleophilic attack at the silicon atom bound to D, displacing the donor molecule and forming the azadisiletine. Tautomerization gives the enamine.



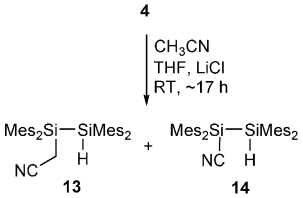
Scheme 3. Proposed mechanism for the formation of the 1,2,3-azadisiletines and tautomers

In contrast, the formation of a ketenimine (**9**) was observed in the addition of phenylacetonitrile to disilene **4** in addition to an enamine analogous in structure to **7** (and **8**). Again, the reaction likely begins with coordination of a donor molecule (D = THF or phenylacetonitrile) to the disilene (Scheme 4). However, in this case, formation of the ketenimine, either intramolecularly (not shown) or intermolecularly, appears to be competitive with cyclization perhaps because of the increased acidity of the α-hydrogen atoms in phenylacetonitrile. Furthermore, the cycloadduct, 1,2,3-azadisiletine **12**, apparently undergoes rapid tautomerization to give enamine **10**, as it was not observed as a product. The rate of tautomerization of **12** to **10** appears to be faster than the rearrangement of **5** to **7** (or of **6** to **8**) most likely because of the increased acidity of the benzylic hydrogen atoms. Of the reactions examined in this study, the addition of phenylacetonitrile to the disilene is the only example in which two distinct types of nitrile adducts are formed.

The rate of addition of a variety of nitriles to bis[bis(trimethylsilyl)methyl]germylene ($[(Me_3Si)_2CH]_2Ge$:) in THF at room temperature increased significantly in the presence of trace



Scheme 4. Proposed mechanism for the formation of compounds **9**, **10** and **12**



Scheme 5. Addition of CH_3CN to disilene **4** in the presence of LiCl

amounts of salts, such as LiCl,[22] and, therefore, LiCl was added to the reaction mixture containing acetonitrile and disilene **4**. The addition of excess CH_3CN to disilene **4** dissolved in THF in the presence of a catalytic amount of LiCl gave a mixture of **13** and **14** in a ratio of about 9:1 at room temperature (Scheme 5). The addition of propionitrile to **4** was attempted under the same reaction conditions; however, **14** was the only nitrile addition product isolated. The structure of **14** was verified by independent synthesis by the addition of KCN to disilene **4** in THF at room temperature followed by subsequent exposure to atmospheric moisture.

The molecular structure of **13** was determined unambiguously by X-ray crystallography (Figure 2). The Si–Si bond length of 2.3866(8) Å is longer than the typical Si–Si single bond length of 2.34 Å[23] and the Si(1)–C40 bond length of 1.938(2) Å is longer than the typical Si–C single bond length of 1.87 Å.[23] The elongated Si–Si and Si–CH_2 bonds are undoubtedly due to the presence of four bulky mesityl substituents. All other bond lengths and angles fall within normal ranges.

The addition of LiCl alters the mode of addition of nitriles to **4** from cycloaddition to α-CH insertion. Notably, CH insertion adducts were also obtained in the addition of nitriles to $[(Me_3Si)_2CH]_2Ge$: in the presence of LiCl.[22] However, in contrast, the same reactions proceeded at room temperature in the absence of salt, albeit at a much slower rate.[22] There is one report in the literature in which a lithium halide (LiBr) assists in the generation of silylenes from a disilene (ArBrSi=SiBrAr, in which Ar = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl) and alters the product of thermolysis[24] giving precedent to our observations.

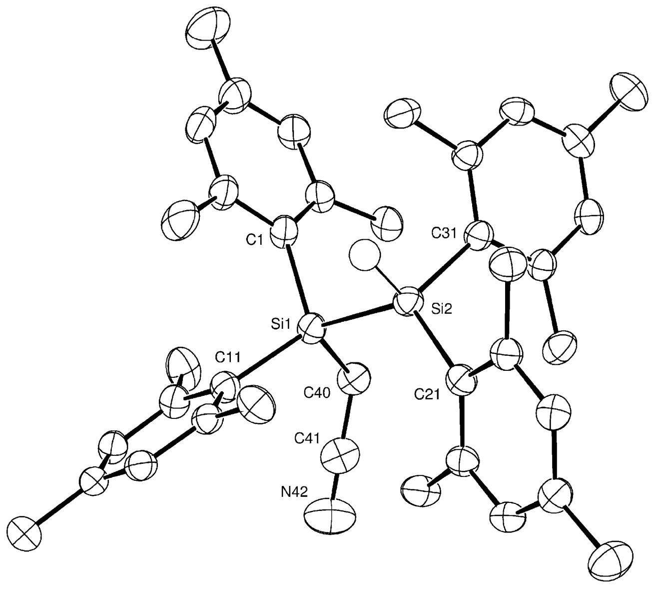
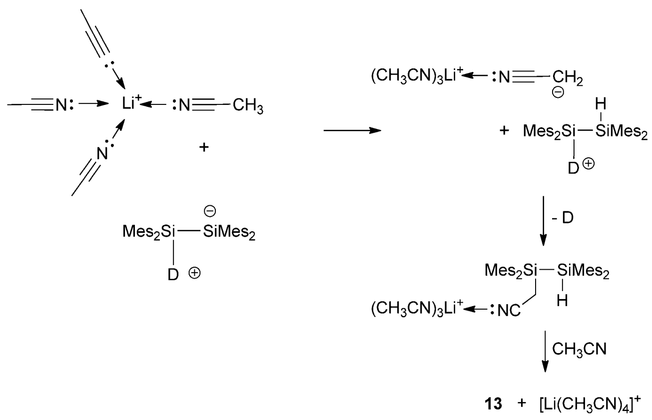


Figure 2. Molecular structure of **13** (50 % probability level). All hydrogen atoms, with the exception of the Si-H, are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–C11 = 1.908(2), Si1–C1 = 1.910(2), Si1–C40 = 1.938(2), Si1–Si2 = 2.3866(8), Si2–C21 = 1.898(2), Si2–C31 = 1.900(2), C40–C41 = 1.454(3), C41–N42 = 1.144(3), C11-Si1-C1 = 111.01(9), C11-Si1-C40 = 104.61(10), C1-Si1-C40 = 108.02(10), C1-Si1-Si2 = 102.50(7), C11-Si1-Si2 = 119.78(7), C21-Si2-C31 = 111.38(8), C21-Si2-Si1 = 124.22(7), C31-Si2-Si1 = 106.91(6), C41-C40-Si1 = 116.1(2), N42-C41-C40 = 179.0(3).

LiCl forms a complex with acetonitrile, in which a Li^+ ion is coordinated to the nitrile group of four acetonitrile molecules in a tetrahedral arrangement.[25] It is plausible that complexation enhances the acidity of the acetonitrile. We postulate the following mechanism for the formation of **13**. After initial coordination of a donor (THF, the nitrile or chloride[26]) to the disilene, abstraction of an α-H from a coordinated CH_3CN would produce the CH_2CN anion (coordinated to Li^+), which can rebound, displacing the donor on silicon (Scheme 6). Ac-



Scheme 6. Proposed mechanism for the formation of **13**

cordingly, the addition of CD_3CN to disilene **4** in THF in the presence of LiCl produced $Mes_2Si(CD_2CN)Si(D)Mes_2$ (**13′**), $Mes_2Si(CN)Si(D)Mes_2$ (**14′**), (and a mesityl-containing unknown compound) in a ratio of approximately 1:1.5,[27] consistent with our proposal.

The addition of CH_3CN to disilene **4** in the presence of LiCl resulted in the formation of small amounts of silyl cyanide **14**, which was formed in significant quantities when CH_3CH_2CN was added to the disilene. Although KCN reacted with **4** to give **14**, the presence of either HCN or a cyanide salt in the acetonitrile or propionitrile is unlikely; the acetonitrile was purified by passage through a column of alumina and degassed prior to use and the propionitrile was distilled from CaH_2 and degassed. Cleavage of the (iso)nitrile functional group has been observed in the addition of (iso)nitriles to other low valent Group 14 compounds.[21,28] Further work is necessary to understand the formation of compound **14**. Nonetheless, the apparent C–C bond activation demonstrated in these reactions is very interesting and will be explored.

Reactivity studies

Given the potential of surface nitrile adducts to serve as linkers for biological molecules, we performed some preliminary studies on the reactivity of the molecular adducts. We began with the investigation of the reactivity of silyl acetonitrile **13**. Specifically, we were interested in converting the nitrile group of **13** to a carboxylic acid or an amine, as these functional groups are useful in synthesis. Nitriles can typically be hydrolyzed to carboxylic acids by treatment of the compound with dilute aqueous acid or base at elevated temperatures;[29] alternatively, nitriles can be reduced to amines using $LiAlH_4$.[29] In general, silyl acetonitriles (R_3SiCH_2CN) are useful reagents in synthesis.[30–32] The nitrile group within a silyl acetonitrile increases the acidity of the α-hydrogen atoms, but also increases the susceptibility of the compound to Si–C cleavage by nucleophilic attack at silicon.[33,34] The weakened Si–C bond is often taken advantage of in synthesis; however, this property also makes it difficult to modify the nitrile groups of silyl acetonitriles without the formation of silanol (R_3SiOH) derivatives. In fact, there are no reports of the hydrolysis or reduction of a nitrile group within a silyl acetonitrile.

Reactivity studies revealed that **13** is relatively stable under a variety of conditions: in the presence of acid, only small amounts of mesitylene were formed and, in the presence of base, no reaction was observed. In reaction with excess $LiAlH_4$, only small amounts of $(Mes_2SiH)_2$ and Mes_2SiH_2 were isolated. The formation of $(Mes_2SiH)_2$ and Mes_2SiH_2 suggests that the CH_2CN group of **13** is susceptible to cleavage under these conditions.

In comparison, silyl acetonitriles $(Mes_2SiH)_2(CHCN)$ (**15**) and $Mes_2SiH(CH_2CN)$ (**16**) are stable towards acid; however, in contrast to **13**, cleavage of the Si–CH_x bonds of **15** and **16** occurs rapidly and nearly quantitatively in the presence of base at room temperature to give $Mes_2SiH(OH)$.[34] The C–C bond lengths within the CH_xCN moiety of **13** and **15** are similar (1.454(3) and 1.460(3) Å,[34] respectively) and the C≡N bonds of **13** and **15** are identical in length. However, the Si–CH_2 bond length of **13** (1.938(2) Å) is slightly longer than the two Si–CH bond lengths of 1.929(2) and 1.917(2) Å in **15** likely because of steric crowding. In **15**, the CHCN moiety acts as a spacer between the two Mes_2SiH groups which relieves crowding within the molecule. Clearly, the reduction of steric congestion in **15** and **16** increases their susceptibility towards hydrolysis under basic conditions, which is more consistent with the reactivity of typical silyl acetonitriles.[33,34] As the molecular structure of **13** indicates, the CH_2CN moiety is situated between two bulky mesityl groups (Figure 2). In contrast to less hindered silyl acetonitriles, the closely spaced mesityl groups of **13** appear to protect the nitrile group from further reaction and protect the silicon center from nucleophilic attack.

Ketenimine **9** hydrolyzes cleanly to the amide **11** upon chromatography, exposure to the ambient atmosphere or under acidic conditions. The azadisiletine **5** and **6** and their enamine tautomers (**7** and **8**) decompose to a mixture of products upon exposure to the ambient atmosphere; the mixtures were not separated.

Comparison between the disilene-acetonitrile adducts and the acetonitrile adducts on the Si(100)-2×1 surface

Our studies indicate that disilene **4** and the Si(100)-2×1 surface are similar in reactivity towards acetonitrile. Despite the significant differences in the reaction conditions, α-CH insertion adducts (**13** and **1**) and cycloadducts (**5** and **2a**,**b**) are formed in both instances. In contrast, a ketenimine was not observed in the addition of acetonitrile to disilene **4**, although one was observed on the surface. The formation of the products in the molecular system appears to be dependent on the polarization of the Si=Si bond through coordination of a donor molecule (either THF/nitrile or LiCl) to the disilene. The α-CH insertion is only observed in the presence of LiCl; coordination of THF or the nitrile apparently is not sufficient for the abstraction of an α-hydrogen atom. The formation of a ketenimine in the molecular system appears to rely on the enhanced acidity of the α-CH bond in the nitrile as in phenylacetonitrile; no ketenimine was formed in the addition of acetonitrile to disilene **4**. On the surface, the Si=Si dimers are not static, they rapidly tilt back and forth polarizing the Si=Si bond[1] and this motion appears to enable the formation of α-CH insertion (**1**), cycloaddition (**2a**,**b**), and ketenimine derivatives (**3a**,**b**) without donor molecules.

Of the three types of adducts formed on the Si surface, only the α-CH insertion adduct (**1**) has been identified unambiguously.[2–7] However, all of the structures of molecular adducts were established unambiguously using spectroscopic techniques. Although the majority of the characterization data obtained for **13** cannot be compared to the data obtained for **1**, the FTIR spectroscopic data of **13** can be directly compared to the MIR-FTIR spectroscopic data of **1**. The wavenumber of the absorption assigned to the C≡N stretching vibration of **13** ($2235\,cm^{-1}$) is quite similar to that assigned to the C≡N stretching vibration in **1** ($2228\,cm^{-1}$).[3,7] Given the limitations of the techniques available to characterize surface adducts, the exact structure of surface adduct **2** could not be established.[2–7] Two structures for **2** have been proposed: an 1,2,3-azadisiletine, formed by the reaction between the $C{\equiv}N$ bond of acetonitrile and the $Si{=}Si$ bond of the dimer (**2a**), and a cycloadduct containing a $CH_2CH{=}N$ moiety within a five-membered ring (**2b**) (Figure 1). On the basis of our results, we believe that **2a** is the correct structure and that **2b** is not present. Finally, we propose that a ketenimine similar in structure to **9**, without a bond between the surface and the terminal carbon, is more reasonable and may indeed be the actual species present on the surface (Figure 3).

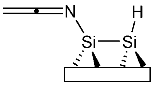


Figure 3. Proposed structure for the surface ketenimine

The acetonitrile adducts formed on the Si(100)-2×1 surface may be modified to allow for the attachment of another layer of organic molecules. However, since three types of adducts are formed on the Si surface, which cannot be separated from one another, modifying the surface by simple chemical procedures may lead to a complex mixture. It is, therefore, instructive to understand the reactivity of the molecular adducts prior to modification of any surfaces. Since molecular adducts are similar in structure to surface adducts, the reactivity of the adducts should also be comparable. Silyl acetonitrile **13** was unreactive towards acid, base, or $LiAlH_4$; the mesityl substituents appear to protect the $SiCH_2CN$ moiety from further reaction. Although silyl acetonitriles **15** and **16** contain more accessible nitrile groups than **13**, they appear to be unreactive towards acid as well, since **15** and **16** are isolated under acidic conditions. However, the intentional hydrolysis of the nitrile groups of **15** and **16** under acidic conditions has not been investigated.[34] Under basic conditions, the $Si{-}CH_xCN$ bonds of **15** and **16** are readily cleaved[34] and the Si–CH bonds of simple silyl acetonitriles are cleaved under both acidic and basic conditions;[34] thus, hydrolysis of the nitrile group within a silyl acetonitrile has not been observed previously. The nitrile group of surface adduct **1** may be more reactive than the nitrile group within **13**; the bonds to the bulk crystal are pinned back in a *cis* fashion which exposes the CH_2CN group on the surface. Given that silyl acetonitriles are more susceptible to cleavage of the Si–CH bond than to hydrolysis of the nitrile group, we believe that attempted hydrolysis of the nitrile group of **1** may simply result in cleavage of the CH_2CN group from the surface.

On the basis of the observed decomposition of the 1,2,3-azadisiletines and their enamine tautomers under ambient conditions, it is unlikely that the hydrolysis of the analogous compounds on the surface (i.e., **2a**) will be clean and lead to a single product. In contrast, the hydrolysis of a surface ketenimine (as in Figure 3) may cleanly lead to an amide or directly to an amine on the surface which could be utilized for the attachment of more complex molecules. To achieve the clean formation of a ketenimine on the surface, we propose the use of phenylacetonitrile.

Conclusion

The α-CH insertion products and cycloadducts were formed by the addition of nitriles to $Mes_2Si{=}SiMes_2$ (**4**); the outcome depended upon the nature of the nitrile and the reaction conditions. In THF, in the absence of salt, nitriles reacted with **4** through the $C{\equiv}N$ bond to give 1,2,3-azadisiletines. Enamines were also observed and likely formed by tautomerization of the initial cycloadducts. With phenylacetonitrile, a ketenimine was formed as a major product rather than an azadisiletine. The change in reactivity was attributed to the enhanced acidity of the α-hydrogen atoms in phenylacetonitrile. In the presence of LiCl, acetonitrile and propionitrile added to the disilene to give an α-CH insertion product (**13**) and/or the formal HCN adduct of the disilene (**14**).

Unlike typical silyl acetonitriles, $Mes_2Si(CH_2CN)Si(H)Mes_2$ (**13**) was stable under a variety of conditions likely due to the presence of four bulky mesityl substituents. On the other hand, the phenylacetonitrile adduct of disilene **4**, that is, ketenimine **9**, rapidly hydrolyzed and rearranged in the presence of acid to give silyl amide **11**. 1,2,3-Azadisiletines and their enamine tautomers were susceptible to uncontrolled hydrolysis under the ambient atmosphere.

Since the acetonitrile adducts formed on the Si(100)-2×1 surface were similar in structure to those formed by the addition of acetonitrile to disilene **4**, the reactivity of the molecular adducts was investigated to gain some insight into the possible reactivity of the surface adducts. Silyl acetonitrile **13** is analogous in structure to surface adduct **1**; however, the bulky mesityl substituents within **13** reduced the reactivity of the nitrile group, and thus, **13** could not be used as a molecular model for surface adduct **1**. The CH_2CN moiety of **1** is more exposed on the surface, which may lead to increased reactivity of the nitrile group; however, previous results suggest that only cleavage of the $Si{-}CH_2CN$ bond will occur on the surface if hydrolysis of the nitrile group is attempted.[34] As an alternative, reduction of the nitrile group of **1** using H_2/W may be successful.[35] 1,2,3-Azadisiletine **5** is structurally similar to surface adduct **2a**; both adducts appear to contain an exposed $C{=}N$ bond. Thus, **5** may be comparable in reactivity to **2a**; however, our results suggest that the hydrolysis of **5** will not be straightforward although the reactivity of **5** needs to be examined in greater detail. The addition of phenylacetonitrile to the surface should be examined as the enhanced acidity of the α-hydrogen atoms may lead to a cleaner reaction and an adduct that is easily and cleanly hydrolyzed in a subsequent step.

Interestingly, Hamers has recognized that the degree of zwitterionic character of a Group 14 (001) surface dimer, achieved by the tilting of the dimers on the surface, can strongly influence the reaction pathway.[36] Herein, we have reported that the use of a simple salt (i.e., LiCl) can alter the course of a reaction of a disilene. The use of donor molecules to enhance or alter reactivity is a concept that has not been widely recognized or exploited in disilene chemistry although there have been a few scattered reports which indicate that the use of a donor to influence a reaction pathway may be more widely applicable.[21,24] We intend to explore this concept more fully.

Experimental Section

Addition of CH_3CN to disilene 4: A deep yellow solution of **4** (made from $Mes_2Si(SiMe_3)_2$ (50 mg, 0.12 mol) and dissolved in THF (8 mL)) and CH_3CN (1 mL, excess) was heated in a sealed Schlenk tube in an oil bath at 100 °C for 24 h; the deep yellow solution decolorized to very pale yellow. Analysis of an aliquot by ^1H NMR spectroscopy revealed the presence of **5** and **7** in a ratio of $>10:1$. The relative amount of **7** in solution increased slowly under an inert atmosphere and, upon exposure to trace amounts of atmospheric moisture (sample in an NMR tube sealed only with Parafilm), the relative amount of **7** appeared to increase more rapidly. Exposure to atmospheric moisture led to decomposition of **5** and **7**, and therefore, they were not separated prior to characterization. NMR spectral data for **5** were obtained from a solution containing **5** and **7** in a ratio of about 8:1. NMR spectral data for **7** were obtained from a solution containing **5** and **7** in a ratio of about 1:5. Solutions of **5** and **7** were contaminated with a minor amount of impurities. High-resolution EI-MS for $C_{38}H_{47}Si_2N$ [M^+]: *m/z* calcd: 573.3247; found: 573.3225.

Data for **5**: ^1H NMR (C_6D_6, 600 MHz): $\delta = 6.69$ (s, 4H; Mes *m*-H), 6.64 (s, 4H; Mes *m*-H), ~2.8–2.2 (v br s, Mes *o*-CH_3), 2.55 (s, CH_3; total 15H), 2.22 (s, 12H; Mes *o*-CH_3), 2.08 (s, 6H; Mes *p*-CH_3), 2.06 ppm (s, 6H; Mes *p*-CH_3); ^{13}C NMR (C_6D_6, 150 MHz): $\delta = 214.76$ (C=N), ~144.8 (v br, Mes *o*-C), 143.71 (Mes *o*-C), 139.22 (Mes *p*-C), 139.13 (Mes *p*-C), 133.77 (Mes *i*-C), 133.25 (Mes *i*-C), ~129.4 (br, Mes *m*-C), 129.29 (Mes *m*-C), 33.35 (CH_3), 24.5 (Mes *o*-CH_3), 24.35 (Mes *o*-CH_3), 21.03 (Mes *p*-CH_3), 20.99 ppm (Mes *p*-CH_3); ^{29}Si NMR (C_6D_6): $\delta = 8.1$, 7.0 ppm.

Data for **7**: ^1H NMR (C_6D_6, 600 MHz): $\delta = 6.66$ (s, 4H; Mes *m*-H), 6.64 (s, 4H; Mes *m*-H), 4.70 (s, 1H; =CH_{cis}), 4.62 (s, 1H; =CH_{trans}, $^3J_{SiH} =$ 12 Hz), 4.53 (s, 1H; NH, $^3J_{SiH} = 25$ Hz), 2.42 (s, 12H; Mes *o*-CH_3), 2.29 (s, 12H; Mes *o*-CH_3), 2.06, 2.05 ppm (both s, 12H; Mes *p*-CH_3); ^{13}C NMR (C_6D_6, 150 MHz): $\delta = 160.17$ (=C-NH), 144.55 (Mes *o*-C), 143.77 (br, Mes *o*-C), 138.86 (Mes *p*-C), 138.85 (Mes *p*-C), 135.73 (br, Mes *i*-C), 132.98 (Mes *i*-C), 129.43 (Mes *m*-C), 129.29 (Mes *m*-C), 92.95 (=CH_2), 24.55 (Mes *o*-CH_3), 24.47 (Mes *o*-CH_3), 21.02 (Mes *p*-CH_3), 20.99 ppm (Mes *p*-CH_3); ^{29}Si NMR (C_6D_6): $\delta = 0.5$ (Mes_2SiN), -6.7 ppm (Mes_2SiC).

Tautomerization of 5 to 7: Half of a mixture containing **5** and **7** (ratio of 10:1) was dissolved in C_6D_6 (0.6 mL) and the other half was dissolved in [D_8]THF (0.6 mL). The solutions were transferred to Teflon screw-capped NMR tubes (J. Young tubes) and heated in an oil bath at 100 °C overnight (ca. 17 h) to give **5** and **7** in a ratio of about 1:1 in both solutions, as estimated by ^1H NMR spectroscopy. Additional heating resulted in a slow increase in the relative amount of **7** in both solutions until **5** and **7** were present in a ratio of about 1:2 (C_6D_6) and about 1:1.5 ([D_8]THF).

Addition of CH_3CH_2CN to disilene 4: A deep yellow solution of **4** (made from $Mes_2Si(SiMe_3)_2$ (50 mg, 0.12 mol) and dissolved in THF (8 mL)) and CH_3CH_2CN (1 mL, excess) was heated in a sealed Schlenk tube in an oil bath at 100 °C for 12 h; the deep yellow solution decolorized to very pale yellow. The solvent was removed under vacuum; a pale yellow solid was obtained. The crude product was analyzed by ^1H NMR spectroscopy; **6** was the only nitrile adduct observed. The crude solid was then washed twice with hexanes to remove impurities, including small amounts of $(Mes_2SiH)_2$[37] and Mes_2SiH_2.[38,39] The remaining solvent was removed under vacuum; a white solid was obtained. ^1H NMR spectroscopic analysis of the purified product revealed the presence of **6** and two diastereomers of **8** (**a** and **b**) in a ratio of about 19:2:1. Exposure of the solution to trace amounts of atmospheric moisture (sample in an NMR tube sealed only with Parafilm) resulted in an increase in the relative amount of **8** until **6**, **8a**, and **8b** were present in a ratio of about 1:7:1 as estimated by ^1H NMR spectroscopy. Compounds **6** and **8** decomposed upon prolonged exposure to atmospheric moisture; therefore, **6** and **8** were characterized as a mixture. NMR spectral data for **6** were obtained from a solution containing **6** and **8a/b** in a ratio of about 6:4:1. NMR spectral data for **8** were obtained from a solution containing **6** and **8a/b** in a ratio of about 1:7:1. High-resolution EI-MS for $C_{39}H_{49}Si_2N$ [M^+]: *m/z* calcd: 587.3404; found: 587.3403.

Data for **6**: ^1H NMR (C_6D_6, 400 MHz): $\delta = 6.69$ (s, 4H; Mes *m*-H), 6.65 (s, 4H; Mes *m*-H), 2.87 (q, 2H; CH_2, $J = 7$ Hz), ~2.7–2.4 (v br s, 12H; Mes *o*-CH_3), 2.23 (s, 12H; Mes *o*-CH_3), 2.07 (s, 6H; Mes *p*-CH_3), 2.06 (s, 6H; Mes *p*-CH_3), 1.23 ppm (t, 3H; CH_3, $J = 7$ Hz); ^{13}C NMR (C_6D_6, 100 MHz): $\delta = 217.12$ (C=N), ~144.8 (v br, Mes *o*-C), 143.71 (Mes *o*-C), 139.19 (Mes *p*-C), 139.06 (Mes *p*-C), 133.87 (Mes *i*-C), 133.53 (Mes *i*-C), 129.44 (br, Mes *m*-C), 129.28 (Mes *m*-C), 38.07 (CH_2), 24.53 (Mes *o*-CH_3), 24.38 (Mes *o*-CH_3), 21.03 (Mes *p*-CH_3), 21.00 (Mes *p*-CH_3), 9.50 ppm (CH_3); ^{29}Si NMR (C_6D_6): $\delta = 7.7$ ppm (Mes_2SiN, Mes_2SiC).[40]

Data for **8**: ^1H NMR (C_6D_6, 600 MHz): $\delta = 6.67$ (s, 4H; Mes *m*-H), 6.65 (s, 4H; Mes *m*-H), 5.15 (q, 1H; =CH, $J = 7$ Hz, **a**), 5.05 (q, 1H; =CH, $J = 7$ Hz, **b**), 4.56 (s, 1H; NH, $^3J_{SiH} = 24$ Hz, **a**), 4.21 (s, 1H; NH, $^3J_{SiH} =$ 25 Hz, **b**), 2.40 (s, 12H; Mes *o*-CH_3), 2.34 (s, 12H; Mes *o*-CH_3), 2.06 (s, 12H; Mes *p*-CH_3), 1.69 (d, 3H; CH_3, $J = 7$ Hz, **b**), 1.56 ppm (d, 3H; CH_3, $J = 7$ Hz, **a**); ^{13}C NMR (C_6D_6, 100 MHz): $\delta = 151.52$ (=C-NH), 144.47 (Mes *o*-C), 143.74 (Mes *o*-C), 138.74 (Mes *p*-C), 138.70 (Mes *p*-C), 136.15 (Mes *i*-C), 133.41 (Mes *i*-C), 129.43 (Mes *m*-C), 129.27 (Mes *m*-C), 103.79 (=CH, **b**), 102.06 (=CH, **a**), 24.53 (Mes *o*-CH_3), 24.22 (Mes *o*-CH_3), 21.01 (Mes *p*-CH_3), 21.00 (Mes *p*-CH_3), 16.58 (CH_3, **b**), 11.28 ppm (CH_3, **a**); ^{29}Si NMR (C_6D_6): $\delta = 1.5$ (Mes_2SiN, **a**), 0.7 (Mes_2SiN, **b**), -7.1 (Mes_2SiC, **a**), -11.5 ppm (Mes_2SiC, **b**).

Addition of $PhCH_2CN$ to disilene 4: A deep yellow solution of **4** (made from $Mes_2Si(SiMe_3)_2$ (51 mg, 0.12 mol) and dissolved in THF (5 mL)) and $PhCH_2CN$ (26 mg, 0.22 mmol) was stirred at room temperature for 48 h, then the solvent was removed under vacuum; a bright yellow oil was obtained. ^1H NMR spectroscopic analysis of the crude product revealed the presence of **9** and **10** in a ratio of about 5:1, as well as a small amount of impurities and unreacted $PhCH_2CN$; **9** and **10** were characterized as a mixture. Separation of the mixture by preparative thin-layer chromatography (silica gel, 1:1 CH_2Cl_2/hexanes) yielded a white solid (11 mg, 26%) identified as **11**, which was contaminated with about 4% of a mesityl-containing unknown and silicone grease. Compounds **9** and **10** were not recovered from the chromatographic plate. Data for **9** and **10**: IR (thin film): $\tilde{\nu} = 2100\ cm^{-1}$ (SiH and N=C=C); high-resolution EI-MS for $C_{44}H_{51}Si_2N$ [M^+]: *m/z* calcd: 649.3560; found: 649.3534.

Data for **9**: ^1H NMR (C_6D_6, 600 MHz): $\delta = 7.14$–7.09 (m, 2H; Ph *m*-H), 7.04–7.00 (m, 2H; Ph *o*-H), 6.88–6.83 (m, 1H; Ph *p*-H), 6.69 (s, 4H; Mes *m*-H), 6.63 (s, 4H; Mes *m*-H), 5.78 (s, 1H; SiH, $^1J_{SiH} = 184$ Hz, $^2J_{SiH} = 11$ Hz), 4.17 (s, 1H; =CHPh), 2.33 (v br s, Mes *o*-$CH_3 \times 2$), 2.08 (s, 6H; Mes *p*-CH_3), 2.04 (s, 6H; Mes *p*-CH_3) ppm; ^{13}C NMR (C_6D_6, 150 MHz): $\delta = 175.04$ (N=C=C), 145.42 (Mes *o*-C), 144.70 (Mes *o*-C), 139.80 (Mes *p*-C), 139.26 (Mes *p*-C), 137.40 (Ph *i*-C), ~131.3 (br, Mes *i*-C), 129.94 (br, Mes *i*-C, Mes *m*-C), 129.28 (Mes *m*-C), 128.98 (Ph *m*-C), 123.97 (Ph *o*-C), 122.22 (Ph *p*-C), 42.64 (N=C=CHPh), 24.30 (br, Mes *o*-$CH_3 \times 2$), 21.06 (Mes *p*-CH_3), 20.96 ppm (Mes *p*-CH_3); ^{29}Si NMR (C_6D_6): $\delta = -24.7$ (Mes_2SiN), -55.1 ppm (Mes_2SiH).

Data for **10**: ^1H NMR (C_6D_6, 600 MHz): $\delta = 7.33$–7.29 (m, 2H; Ph *o*-H), 7.21–7.16 (m, 2H; Ph *m*-H), 7.00–6.96 (m, 1H; Ph *p*-H), 6.68 (s, Mes *m*-H), 6.60 (s, 4H; Mes *m*-H), 6.16 (s, 1H; =CHPh), 6.15 (br s, 1H; NH, $^3J_{SiH} = 24$ Hz),[41] 2.45 (s, Mes *o*-CH_3), 2.30 (s, Mes *o*-CH_3), 2.07 (s, Mes *p*-CH_3), 2.03 ppm (s, Mes *p*-CH_3); ^{13}C NMR (C_6D_6, 150 MHz): $\delta = 154.16$ (=C-NH), ~144.7 (br, Mes *o*-C), 143.83 (Mes *o*-

C), 139.72 (Ph *i*-C), 139.05 (Mes *p*-C),[42] 139.00 (Mes *p*-C),[42] 135.33 (Mes *i*-C), 132.59 (Mes *i*-C), 129.52 (Mes *m*-C), 129.45 (Mes *m*-C), 128.98 (Ph *m*-C), 127.48 (Ph *o*-C), 124.81 (Ph *p*-C), 108.86 (=CHPh), 24.77 (Mes *o*-CH$_3$), 24.39 (Mes *o*-CH$_3$), 21.03 (Mes *p*-CH$_3$), 20.96 ppm (Mes *p*-CH$_3$); ^{29}Si NMR (C$_6$D$_6$): $\delta = 4.0$ (Mes$_2$SiN), -4.1 ppm (Mes$_2$SiC).

*Data for **11***: White solid; ^{1}H NMR (C$_6$D$_6$, 600 MHz): $\delta = 7.05$–6.93 (m, 5 H; Ph), 6.70 (s, 4 H; Mes *m*-H), 6.62 (s, 4 H; Mes *m*-H), 5.75 (s, 1 H; SiH, $^1J_{\mathrm{SiH}} = 184$ Hz), 5.58 (br s, 1 H; NH), 3.46 (s, 2 H; CH$_2$), 2.36 (s, 12 H; Mes *o*-CH$_3$), 2.09 (s, 18 H; Mes *o*-CH$_3$, Mes *p*-CH$_3$), 2.04 ppm (s, 6 H; Mes *p*-CH$_3$); ^{13}C NMR (C$_6$D$_6$, 150 MHz): $\delta = 172.96$ (C=O), 145.44 (Mes *o*-C), 144.23 (Mes *o*-C), 138.88 (Mes *p*-C), 138.81 (Mes *p*-C), 135.86 (Ph *i*-C), 132.61 (Mes *i*-C), 131.17 (Mes *i*-C), 130.04 (Ph *o*-C), 129.89 (Mes *m*-C), 129.18 (Ph *m*-C), 129.13 (Mes *m*-C), 127.26 (Ph *p*-C), 47.23 (CH$_2$), 24.77 (br, Mes *o*-CH$_3$), 24.37 (Mes *o*-CH$_3$), 21.04 (Mes *p*-CH$_3$), 20.91 ppm (Mes *p*-CH$_3$); ^{29}Si NMR (C$_6$D$_6$): $\delta = -18.7$ (Mes$_2$SiN), -54.4 ppm (Mes$_2$SiH); IR: $\tilde{\nu} = 3407$ (w, NH), 3024 (m), 2961 (m), 2920 (m), 2854 (w), 2137 (w, SiH), 1689 (m, C=O), 1604 (m), 1549 (w), 1495 (w), 1452 (m), 1404 (s), 1233 (w), 1061 (w), 1028 (w), 928 (w), 847 (m), 829 (m), 802 (m), 747 (m), 702 (m), 619 (m), 591 (m), 566 (m), 550 cm^{-1} (m); EI-MS: *m/z* (%): 667 (17) [M^+], 652 (25) [M^+-Me], 576 (29) [M^+-PhCH$_2$], 533 (14) [M^+-PhCH$_2$CONH], 400 (75) [M^+-Mes$_2$SiH], 309 (16) [Mes$_2$SiNHCO$^+$], 282 (100) [Mes$_2$SiNH$_2$$^+$], 267 (28) [Mes$_2SiH^+$], 147 (13) [MesSi$^+$], 120 (17) [MesH], 91 (8) [PhCH$_2$$^+$]; high-resolution EI-MS for C$_{44}$H$_{53}$Si$_2$NO [M^+]: *m/z* calcd: 667.3666; found: 667.3646.

Addition of CH$_3$CN to disilene 4 in the presence of LiCl: CH$_3$CN (0.1 mL, 1.9 mmol) was added to a yellow solution of disilene **4** (made from Mes$_2$Si(SiMe$_3$)$_2$ (150 mg, 0.36 mol) and partially dissolved in THF (10 mL)), followed by addition of a solution of LiCl in THF (0.25 mL, 2 mg mL^{-1}, 0.012 mmol). Upon addition of the LiCl solution, the yellow solid began to dissolve and, upon complete dissolution, the yellow color of the solution began to fade. The solution was allowed to stir at room temperature overnight. The solvent was then removed under vacuum and a pale yellow film was obtained. The crude product consisted of four compounds: **13**, **14**, Mes$_2$Si(OH)Si(H)Mes$_2$,[13b] and Mes$_2$Si(Cl)Si(H)Mes$_2$,[13b] in a ratio of about 9:1:1:1, respectively, as estimated by ^{1}H NMR spectroscopy. Preparative thin-layer chromatography (silica gel, 3:7 CH$_2$Cl$_2$-hexanes) of the mixture yielded **13** as a white solid (43 mg, 42 %). Impure **14** was also obtained from the chromatographic plate, but in trace amounts.

*Data for **13***: White solid; m.p. 186–192 °C; ^{1}H NMR (C$_6$D$_6$, 600 MHz): $\delta = 6.66$ (s, 8 H; Mes *m*-H), 5.78 (s, 1 H; SiH, $^1J_{\mathrm{SiH}} = 184$ Hz), 2.54 (s, 2 H; CH$_2$), 2.31 (br s, 12 H; Mes *o*-CH$_3$), 2.10 (br s, 12 H; Mes *o*-CH$_3$), 2.06 and 2.04 ppm (each s, 12 H; total, Mes *p*-CH$_3$); ^{13}C NMR (C$_6$D$_6$, 600 MHz): $\delta = 145.02$ (Mes *o*-C), 144.70 (Mes *o*-C), 139.47 (Mes *p*-C), 139.17 (Mes *p*-C), 131.43 (Mes *i*-C), 130.69 (Mes *i*-C), 130.10 (Mes *m*-C), 129.28 (Mes *m*-C), 118.71 (C≡N), 24.80 (Mes *o*-CH$_3$ × 2), 21.00 (Mes *p*-CH$_3$), 20.89 (Mes *p*-CH$_3$), 8.10 ppm (CH$_2$); ^{29}Si NMR (C$_6$D$_6$): $\delta = -22.8$ (Mes$_2$SiCH$_2$), -54.7 ppm (Mes$_2$SiH); IR: $\tilde{\nu} = 3023$ (m), 2963 (s), 2921 (s), 2856 (m), 2731 (w), 2235 (s, C≡N), 2138 (s, SiH), 1731 (w), 1604 (s), 1549 (m), 1451 (s), 1408 (m), 1377 (m), 1287 (m), 1264 (m), 1235 (m), 1156 (w), 1027 (m), 953 (w), 928 (w), 848 cm^{-1} (m); EI-MS: *m/z* (%): 573 (58) [M^+], 558 (69) [M^+-Me], 453 (18) [M^+-MesH], 306 (34) [M^+-Mes$_2$SiH], 267 (100) [Mes$_2$SiH$^+$], 147 (57) [MesSi$^+$]; high-resolution EI-MS for C$_{38}$H$_{47}$Si$_2$N [M^+]: *m/z* calcd: 573.3247; found: 573.3259; elemental analysis calcd (%) for C$_{38}$H$_{47}$Si$_2$N: C 79.52, H 8.25, N 2.44; found: C 79.65, H 7.99, N 2.69. **Note**: Mes$_2$Si(OH)Si(H)Mes$_2$ was likely formed by the addition of adventitious water to the disilene and Mes$_2$Si(Cl)Si(H)Mes$_2$ was likely formed by the addition of trace amounts of HCl present in the LiCl. The addition of excess LiCl to disilene **4** indeed produced Mes$_2$Si(Cl)Si(H)Mes$_2$.

*Data for **14***:[43] ^{1}H NMR (C$_6$D$_6$, 600 MHz): $\delta = 6.66$ (s, 4 H; Mes *m*-H), 6.59 (s, 4 H; Mes *m*-H), 5.84 (s, 1 H; SiH, $^1J_{\mathrm{SiH}} = 186$ Hz), 2.36 (v br s, 24 H; Mes *o*-CH$_3$), 2.05 (s, 6 H; Mes *p*-CH$_3$), 2.01 ppm (s, 6 H; Mes *p*-CH$_3$); ^{13}C NMR (C$_6$D$_6$, 150 MHz): $\delta = 145.63$ (Mes *o*-C), ~145.41 (v br, Mes *o*-C), 140.24 (Mes *p*-C), 139.65 (Mes *p*-C), 130.00 (br, Mes *m*-C), 129.95 (Mes *i*-C), 129.43 (br, Mes *m*-C), 128.53 (Mes *i*-C), 24.55 (br, Mes *o*-CH$_3$), 21.02 (Mes *p*-CH$_3$), 20.92 ppm (Mes *p*-CH$_3$);[44] ^{29}Si NMR (C$_6$D$_6$): $\delta = -49.7$ (Mes$_2$SiCN), -53.5 ppm (Mes$_2$SiH); Raman: $\tilde{\nu} = 2919$ (s), 2730 (w), 2180 (m, C≡N), 2160 (w, SiH), 1604 (s), 1445 (w), 1379 (m), 1289 (s), 1058 (w), 945 (w), 573 (s), 552 (w), 536 (w), 477 cm^{-1} (w); IR: $\tilde{\nu} = 3023$ (w), 2964 (m), 2919 (m), 2851 (w), 2176 (w, C≡N), 2139 (w, SiH), 1603 (m), 1549 (w), 1449 (m), 1409 (m), 1378 (w), 1288 (w), 1263 (s), 1094 (m), 1063 (m), 1027 (s), 848 (m), 800 (s), 740 (m), 707 (m), 625 (m), 604 cm^{-1} (m); EI-MS: *m/z* (%): 559 (86) [M^+], 544 (64) [M^+-Me], 440 (24) [M^+-Mes], 424 (21) [M^+-Mes$-$Me], 292 (21) [Mes$_2$SiCN$^+$], 267 (100) [Mes$_2$SiH$^+$], 251 (36), 235 (23), 220 (21), 147 (55) [MesSi$^+$], 120 (14); high-resolution EI-MS for C$_{37}$H$_{45}$Si$_2$N [M^+]: *m/z* calcd: 559.3091; found: 559.3072.

Addition of CD$_3$CN to disilene 4 in the presence of LiCl: CD$_3$CN (5 drops) was added to a yellow solution of disilene **4** (made from Mes$_2$Si(SiMe$_3$)$_2$ (210 mg, 0.51 mol) and partially dissolved in THF (10 mL)) followed by LiCl (5 mg), which had been flame dried under vacuum. The yellow solid slowly dissolved and the solution decolorized to clear, pale yellow within 90 min. The solution was stirred at room temperature overnight. The THF and CD$_3$CN were removed under vacuum and C$_6$D$_6$ (ca. 0.7 mL) was added to the light yellow residue to precipitate the LiCl. A clear, yellow solution was obtained after filtering the solution through a cotton plug. ^{1}H NMR analysis of the crude product revealed the presence of Mes$_2$Si(CD$_2$CN)Si(D)Mes$_2$ (**13′**), Mes$_2$Si(CN)Si(D)Mes$_2$ (**14′**), and a mesityl-containing unknown compound in a ratio of ca. 1:1.5:1.4,[27] and other impurities in small amounts, including Mes$_2$Si(OH)Si(H)Mes$_2$ and Mes$_2$Si(Cl)Si(H)Mes$_2$. The mixture was separated by preparative thin-layer chromatography (silica gel, 3:7 CH$_2$Cl$_2$–hexanes). Compound **13′** was isolated as a white solid contaminated with small amounts of a mesityl-containing unknown, as well as trace amounts of other impurities including **13** (13 mg total). Compound **14′** was isolated as a white solid contaminated with **14** and Mes$_2$Si(OH)Si(H)Mes$_2$ (ratio of ca. 13:1:1) (23 mg total). The ^{1}H NMR spectrum of the unknown compound revealed signals at 6.67, 2.48, and 2.06 ppm; however, this compound has not yet been identified.

*Data for **13′***: ^{2}H NMR (C$_6$H$_6$, 92 MHz): $\delta = 5.77$ (SiD), 2.47 ppm (CD$_2$).

*Data for **14′***: ^{2}H NMR (C$_6$H$_6$, 92 MHz): $\delta = 5.85$ ppm (SiD); IR: $\tilde{\nu} = 3024$ (m), 2966 (m), 2922 (m), 2855 (w), 2177 (w, C≡N), 2150 (w), 1604 (s), 1552 (m), 1449 (s), 1409 (m), 1377 (m), 1288 (m), 1265 (m), 1234 (w), 1063 (m), 1028 (m), 848 cm^{-1} (s); EI-MS: *m/z* (%): 560 (100) [M^+], 545 (73) [M^+-Me], 441 (25) [M^+-Mes], 425 (21), 292 (17) [Mes$_2$SiCN$^+$], 268 (95) [Mes$_2$SiD$^+$], 251 (33), 147 (42) [MesSi$^+$], 119 (17) [Mes$^+$].

Addition of H$_2$SO$_4$ to 13: Compound **13** (32 mg, 0.06 mmol) was dissolved in THF (15 mL) and 1 M H$_2$SO$_4$ (10 mL) was added to the solution. The solution was heated in an oil bath at 90 °C overnight then cooled to room temperature and extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layers were dried over MgSO$_4$, filtered, and concentrated. A clear, colorless film was obtained (28 mg). ^{1}H NMR spectroscopic analysis of the crude product revealed the presence of **13** and mesitylene in a ratio of about 13:1, as well as a small amount of impurities.

Addition of NaOH to 13: A mixture of **13** and mesitylene (obtained by the reaction above, 28 mg) was dissolved in THF (15 mL) and then 15% NaOH solution (5 mL) was added. The mixture was heated in an oil bath at 90 °C overnight then cooled to room temperature and extracted with CH_2Cl_2, as described above; a clear, colorless film was obtained (26 mg). The ^1H NMR spectrum of the crude product revealed the presence of unreacted **13** and some impurities.

Addition of $LiAlH_4$ to 13: Compound **13** (43 mg, 0.08 mmol) was dissolved in THF (2 mL) and slowly added by syringe to $LiAlH_4$ (33 mg, 0.9 mmol) suspended in THF (3 mL). The mixture was stirred overnight at room temperature and then slowly quenched with water (ca. 5 mL) then 15% NaOH solution (ca. 5 mL) and extracted with Et_2O (3×10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. ^1H NMR spectroscopic analysis of the crude product revealed the presence of unreacted **13**, $(Mes_2SiH)_2$,[37] and Mes_2SiH_2[38] in a ratio of about 15:1:1 (18 mg total).

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[39] Compounds $(Mes_2SiH)_2$ and Mes_2SiH_2 are often present in trace amounts in the disilene precursor, $Mes_2Si(SiMe_3)_2$, and are commonly observed in reactions involving **4**.

[40] In the ^{1}H-^{29}Si gHMBC spectrum of **6**, both ^{29}Si signals are at the same chemical shift. The sample contained a number of impurities; thus, the assignment is tentative.

[41] The coupling constant was estimated from correlations in the ^{1}H-^{29}Si gHMBC spectrum of **10**.

[42] Due to overlap in the ^{1}H-^{13}C gHMBC spectrum, the assignment is tentative.

[43] A sample of **14** was prepared by the addition of CH_3CH_2CN to disilene **4** in the presence of LiCl and used for characterization purposes.

[44] A signal which could be assigned to a nitrile group was not observed in the ^{13}C NMR spectrum of **14**, even after increasing the delay between pulses to 5 s.

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