Unusual Reactivity of a Disilyne with 4-Dimethylaminopyridine: Formation of an Intramolecularly N-Coordinated Silylene and Its Isomerization to a Zwitterionic Silyl Anion

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ABSTRACT: Reaction of isolable 1,1,4,4-tetrakis[bis-(trimethylsilyl)methyl]-1,4-diisopropyltetrasila-2-yne (**1**) with an equiv amount of 4-dimethylaminopyridine unexpectedly produced the intramolecularly N-coordinated silylene **2** as the primary product. However, **2** was not thermally stable at room temperature in solution and slowly isomerized to silyl anion **3** with a zwitterionic structure via 1,2-hydrogen migration followed by Si—N bond formation.

Scheme 1. Reaction of Disilyne 1 with DMAP To Give 2 and Subsequent Isomerization of 2 To Give Silyl Anion 3

The chemistry of the alkyne analogues of heavier group 14 elements has been dramatically developed in recent years[1] since the isolation of a lead analogue of an alkyne, ArPbPbAr (Ar = 2,6-Tip$_2$C$_6$H$_3$; Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$), by Power's group.[2] In 2004, we[3a] and Wiberg's group[3b] independently reported the synthesis of disilynes with a silicon—silicon triple bond using two very bulky silyl substituents as the protecting groups at the triply bonded Si atoms. An aryl-substituted disilyne[3c] and an unsymmetrically substituted disilyne[3d] have also recently been reported. The structure of disilyne **1**, RSi≡SiR (R = Si^{i}Pr[CH(SiMe$_3$)$_2$]$_2$), shows trans bending of the silicon—silicon triple bond, which results in two nondegenerate occupied π molecular orbitals (MOs) and two unoccupied antibonding π^* MOs.[3a] Because the energy level of the lowest unoccupied MO (LUMO) of disilynes is significantly lowered, the disilynes are very reactive toward alkenes, alkynes, nitriles, alkali metals, alkyllithiums, etc.[4] Very recently, we reported the reaction of disilyne **1** with 1,3,4,5-tetramethylimidazol-2-ylidene (NHC) to give the disilyne—NHC complex R(L)Si=SiR: (R = Si^{i}Pr[CH(SiMe$_3$)$_2$]$_2$; L = NHC), which has a Si=Si double bond and a lone pair of electrons residing on one of the double-bonded Si atoms.[5] This reaction was explained as the result of the strong interaction of the NHC σ electrons with the LUMO (π^*_{in}) of **1**.

Recently, the strong σ-donating ability of NHCs has caused them to be widely used as ligands to stabilize several low-coordinate silicon compounds, such as :Si=Si:,[6a] a silanone with a Si=O double bond,[6b,e,f] and dihalosilylene[6c,d,g] isolated as NHC complexes. Similar to NHC, 4-dimethylaminopyridine (DMAP) can also work to stabilize low-coordinate species.[7] However, the σ-donation strength of DMAP is less than that of NHC. For instance, Driess and co-workers[8] have reported that the silanone derivative R$_2$(L)Si=O (R$_2$ = CH{[C(Me)=N-(aryl)]C(=CH$_2$)N(aryl)}; aryl =2,6-^{i}Pr$_2$C$_6$H$_3$; L = NHC, DMAP) can be isolated by coordination with both NHC and
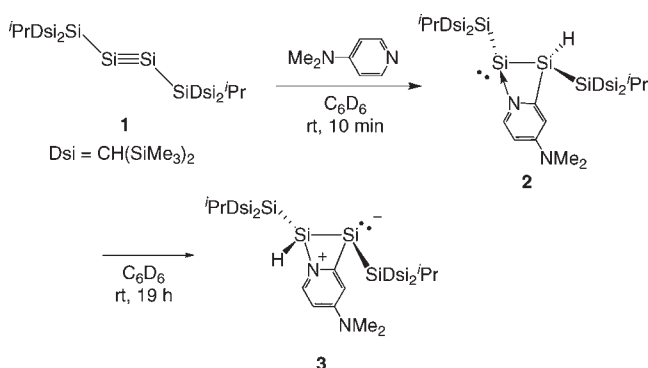
DMAP. However, there is a significant difference in the reactivities of the resulting complexes; the DMAP—silanone complex is able to activate NH$_3$ under mild conditions,[8] whereas the NHC complex cannot do this. The interesting effect that the Lewis basicity of the donor strongly influences the nature of complexes encouraged us to investigate the reaction of disilyne **1** with DMAP. Instead of the formation of a disilyne—DMAP complex, we found that the resulting complex undergoes ortho C—H bond insertion of the pyridyl group to give the intramolecularly N-coordinated silylene **2**, and subsequent 1,2-hydrogen migration and Si—N bond formation occurs, resulting in the formation of the silyl anion **3** with a zwitterionic structure, which we report in this paper.

The reaction of disilyne **1** with 1 equiv of DMAP in benzene proceeded immediately, giving a reddish-brown solution of the intramolecularly N-coordinated silylene **2** (Scheme 1).[9] Although the reaction of disilyne **1** with NHC gave a 1:1 disilyne—NHC complex,[5] this type of compound was not obtained in the present reaction. The N-coordinated silylene **2** was isolated as air- and moisture-sensitive reddish-brown crystals by recrystallization from pentane at −30 °C, and it was characterized by NMR spectroscopic analysis as well as X-ray crystallography.[10] The ^{29}Si NMR spectrum of **2** in C$_6$D$_6$ shows a signal for the silylene Si atom at 59.9 ppm, which is significantly upfield-shifted relative to uncomplexed silylene Si atoms.[11] This chemical shift of the silylene coordinated by the pyridyl group was well-reproduced by GIAO calculations [B3LYP/6-311G(d),
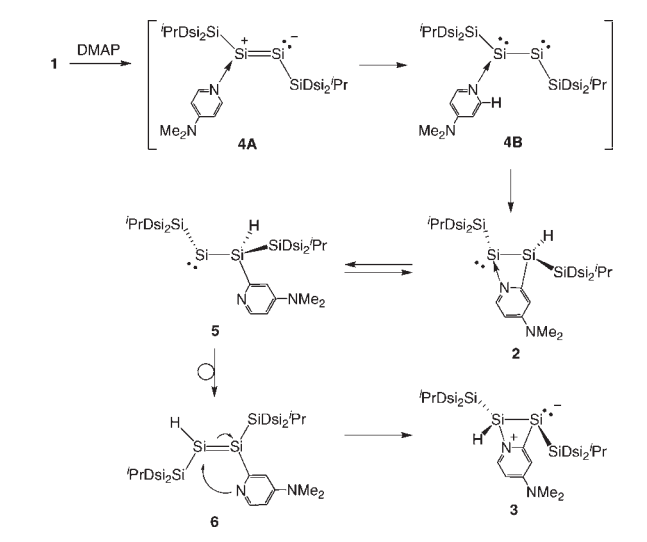
Chart 1. Relative Energies of the Model Compounds 2′, 3′, and 6′ Obtained from DFT Calculations at the B3LYP/6-31G(d) Level

2′	**6′**	**3′**
0.2 kcal/mol	+8.8 kcal/mol	0 kcal/mol
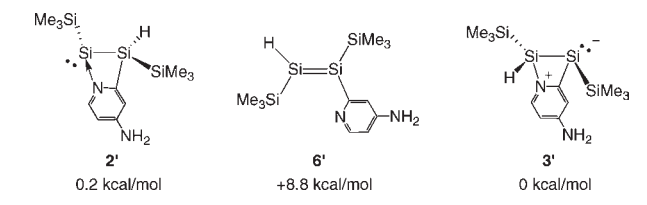
Scheme 2. Plausible Mechanism for the Formation of N-Coordinated Silylene 2 from the Reaction of Disilyne 1 with DMAP and the Subsequent Isomerization of 2 To Give Silyl Anion 3

Figure 1. ORTEP drawing of **3** (50% thermal ellipsoids). Hydrogen atoms (except for Si—H) and crystal solvent molecules (pentane) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1—Si2, 2.4061(11); Si1—Si3, 2.4181(11); Si2—Si4, 2.4248(11); C35—Si2, 1.922(3); N1—Si1, 1.841(2). N1—Si1—Si2, 77.05(8); N1—Si1—Si3, 108.67(8); Si2—Si1—Si3, 130.97(4); C35—Si2—Si1, 71.32(9); C35—Si2—Si4, 112.07(9); Si1—Si2—Si4, 111.65(4).

6-311G(3d) for Si//B3LYP/6-31G(d)] on the model compound **2′** (Me₃Si instead of the Si^{i}Pr[CH(SiMe₃)₂]₂ substituent; Chart 1), which gave a value of 69.9 ppm.

A plausible mechanism for the formation of **2** is depicted in Scheme 2. The reaction of disilyne **1** with DMAP would give the 1:1 complex **4A** as an intermediate, similar to that of the reaction of **1** with NHC.[5] However, the bis-silylene-type resonance structure **4B** might be considered in the present case, and intramolecular insertion of the bis-silylene into a C—H bond of the pyridyl group would then occur, giving the N-coordinated silylene **2**.[12]

Although **2** is stable below −30 °C in hydrocarbon solvents, this compound is thermally unstable and gradually isomerizes to hydrogen-migrated **3** at room temperature (Scheme 1). Complete isomerization of **2** occurred within 19 h at room temperature in C₆D₆, and the isomer **3** was isolated as air- and moisture-sensitive brown crystals.[9]

The molecular structure of **3** is shown in Figure 1. The Si1—Si2 bond length [2.4061(11) Å] is reasonable for a Si—Si single bond. The N1—Si1 length [1.841(2) Å] is significantly shorter than the Si—N distance in the DMAP-coordinated silylene [2.005(2) Å][8] but similar to that of Me₃Si(pyridine)⁺I⁻ [1.858(9) Å].[13] The C35—Si2 bond length in **3** [1.922(3) Å] is slightly longer than typical Si—C(aryl) single bond lengths (av 1.879 Å)[14] but close to that in [Ph(Me₃Si)₂SiLi]₂ [1.939(6) Å].[15a] The sum of the bond
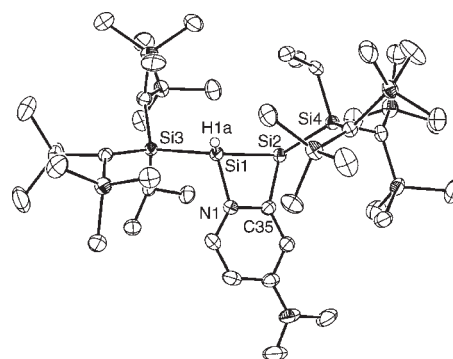
angles around the Si2 atom (295.04°) shows its significant pyramidalization, indicating that the Si2 atom has the silyl anion structure. Because the Si2 atom of **3** has three covalent bonds [two Si—Si bonds and one Si—C(ar) bond] and a lone pair of electrons, **3** is reasonably represented by the silyl anion structure.

The NMR spectral data also support the silyl anion structure of **3**. Thus, the ^{29}Si NMR resonance of the Si atom with the lone pair of electrons in **3** exhibits a signal at −61.5 ppm in C₆D₆, appearing at a higher field than that of **2** (59.9 ppm). Because the ^{29}Si chemical shifts of (aryl)disilyl-substituted silyl anions are observed at high fields (e.g., [Ph(Me₃Si)₂SiLi]₂ = −94.0 ppm,[15a] [Ph(Me₃Si)₂Si)]₂Mg(thf)₂ = −92.5 ppm[15b]), the upfield-shifted ^{29}Si NMR signal of **3** supports its silyl anion structure. The upfield-shifted ^{29}Si NMR chemical shift was reproduced by GIAO calculations [B3LYP/6-311G(d), 6-311G(3d) for Si//B3LYP/6-31G(d)] on the model compound **3′** (Chart 1), which gave a value of −92.7 ppm. The UV—vis spectrum of **3** in a hexane solution shows an absorption at 442 nm (ε = 5500 M^{-1} s^{-1}) with a shoulder at ∼510 nm that can be assigned to the transitions HOMO to LUMO+1 and HOMO to LUMO, respectively (see the Supporting Information).[16] The HOMO involves an n orbital containing the lone pair on the Si2 atom. The LUMO and LUMO+1 correspond to different π^* orbitals on the pyridine moiety.

A plausible mechanism for the isomerization of **2** to **3** is shown in Scheme 2. Because of the relatively weak coordination of the pyridyl group to the silylene Si atom, it is likely that the uncomplexed silylene **5** can be generated in solution. Then **5** may readily undergo isomerization to disilene **6** by 1,2-hydrogen migration. Subsequently, the interaction of the nitrogen of the pyridyl group with the π^* orbital of the Si═Si double bond in **6** leads to the formation of the silyl anion **3**.

To gain insight into the thermodynamic stability of these structural isomers, density functional theory (DFT) calculations [B3LYP/6-31G(d)] were performed, and the relative energies of the model compounds are shown in Chart 1. Among the three structural isomers, **6′** with a Si═Si double bond is the least stable in comparison with **2′** and **3′**. Although the relative energies of **2′** and **3′** are comparable, the irreversible reaction from **6** to **3** leads to the formation of **3** as the final product.

Although a similar formation and isomerization of a silylene was observed in the reaction of disilyne **1** with pyridine, its isomerization was complete within 1 h at room temperature. The instability of the initial product is presumably due to the weaker Lewis basicity of the pyridyl group relative to DMAP. Because weak coordination of the pyridyl group to a silylene Si of the initial product can easily generate an uncomplexed silylene, the isomerization is accelerated. This result is consistent with the proposed mechanism shown in Scheme 2.

In summary, we have reported the unique reactivity of disilyne **1** with DMAP. In contrast to the NHC−disilyne complex, the DMAP−disilyne complex is capable of undergoing intramolecular insertion into the ortho C−H bond of the pyridyl group, giving the N-coordinated silylene **2**, which further undergoes thermal isomerization to accomplish the unprecedented formation of silyl anion **3** via 1,2-hydrogen migration followed by Si−N bond formation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures for **2** and **3**; computational results on the model compounds **2′**, **3′**, and **6′**; MO diagram and energy levels of **3′**; ORTEP drawing of **2**; UV−vis spectral chart for **3**; and crystallographic data for **3**, including atomic positional and thermal parameters (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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