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Accounts

The Chemistry of Disilyne with a Genuine Si–Si Triple Bond: Synthesis, Structure, and Reactivity

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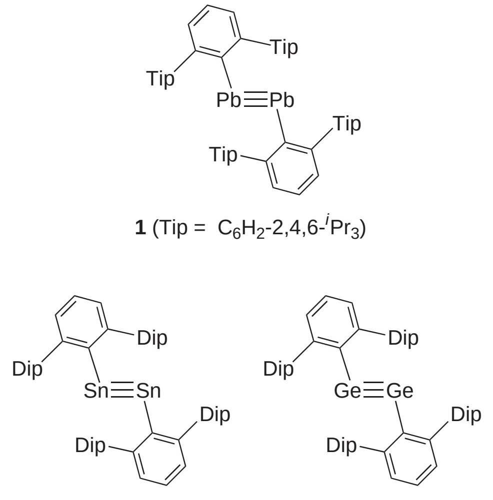
In this account, our recent results on the chemistry of a stable silicon–silicon triply-bonded compound, disilyne, including recent advances in the chemistry of stable alkyne analogues of heavier group 14 elements, are described. Our original extremely bulky trialkylsilyl substituent, $Dis_2{}^iPrSi$ [Dis = $CH(SiMe_3)_2$], has enabled the isolation of disilyne as a stable compound, which has been completely characterized by various spectroscopic techniques, as well as X-ray crystallography. Some reactivity of our isolable disilyne will be discussed.

1. Introduction

The chemistry of stable compounds with multiple bonds of heavier group 14 elements has been studied extensively for more than 30 years, since Lappert and Davidson reported in 1973 the synthesis of the stable distannene $Dis_2Sn{=}SnDis_2$ (Dis = bis(trimethylsilyl)methyl), which has a Sn=Sn double bond in the solid state.[1] The next significant discoveries in the double bond chemistry of heavier group 14 elements came from research groups in 1981; West and colleagues reported the synthesis of a stable compound with a Si=Si double bond, tetramesityldisilene,[2] and Brook et al. synthesized a compound with a Si=C double bond.[3] Thereafter, almost every type of doubly-bonded compound having not only homo- and heteronuclear double bonds between group 14 elements of $>E{=}E'<$ type (E and E′ = C, Si, Ge, Sn, and Pb), but also the double bonds between the heavier group 14 elements and other main group elements (groups 13, 15, and 16) have been synthesized and structurally characterized.[4]

In spite of extensive experimental efforts directed towards the synthesis of triply-bonded compounds of heavier group 14 elements, heavier analogues of alkynes, such as –E≡C– and –E≡E– (E = Si, Ge, Sn, and Pb),[5,6] had remained unknown until recently.[7,8] An epoch-making result in the chemistry of stable heavier analogues of alkynes came in 2000; Power et al. reported the synthesis and structural characterization of the lead analogue of the alkyne **1** (Fig. 1).[9]



1 (Tip = C_6H_2-2,4,6-^{i}Pr$_3$)

2 (Dip = C_6H_3-2,6-^{i}Pr$_2$) **3** (Dip = C_6H_3-2,6-^{i}Pr$_2$)

Fig. 1. Stable lead, tin, and germanium analogues of alkyne drawn with a formal triple bond structure.

Subsequently, tin **2**[10] and germanium **3**[11] analogues were also synthesized by the same group in 2002. The isolation of germanium, tin, and lead analogues of alkynes was achieved by using bulky terphenyl ligands (2,6-diarylphenyl groups), and crystallographic structural determination revealed that **1**–**3** have *trans*-bent structures rather than the linear arrangement of R–E≡E–R. Having formal E≡E triple bonds, these compounds actually exhibited a highly pronounced non-bonding electron density character at the central atoms, resulting in a decrease in the bond order on descending group 14 (Fig. 2).[7a,12] Thus, the bond orders in the *trans*-bent structures of heavier analogues of alkynes are estimated to be 2.32–1.74 (Ge), 1.87–1.73 (Sn), and 1.65–1.51 (Pb) for the model compounds of R–E≡E–R (R = H, Me, and Ph).[7a,13] Higher bond orders (2.20–2.37) were expected for the silicon species.[7a,13]

The first experimental approach to a silicon–silicon triple bond was reported by West and Sekiguchi et al. in 1986.[5a,b]

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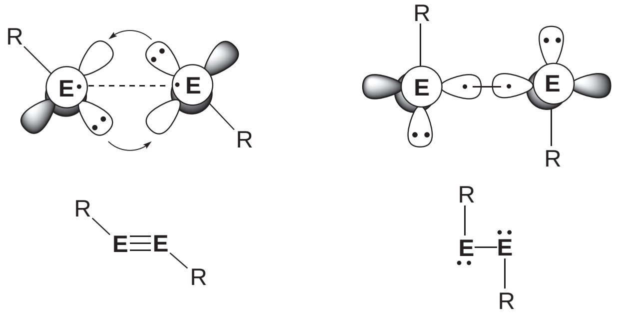
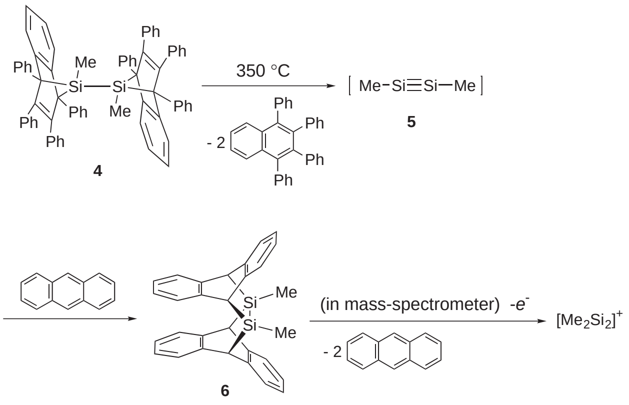
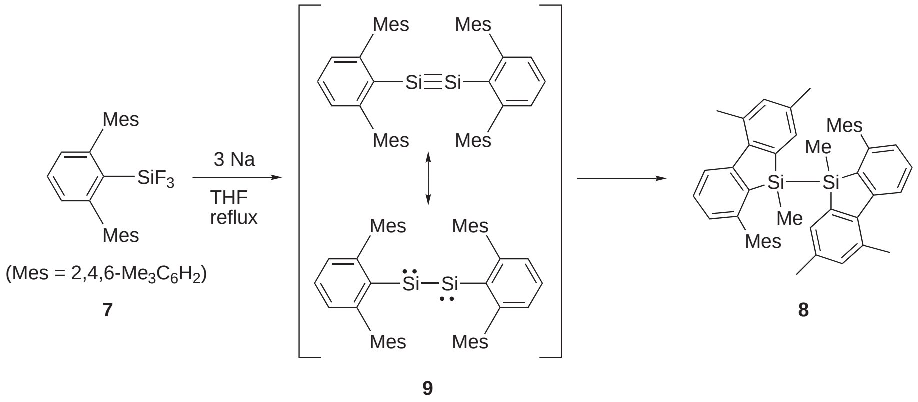


Fig. 2. Bonding model in the *trans*-bent structure of a heavy alkyne. Arrow line, dashed line, and normal line indicate donor–acceptor dative bond, π-bond, and σ-bond, respectively.



Scheme 1.

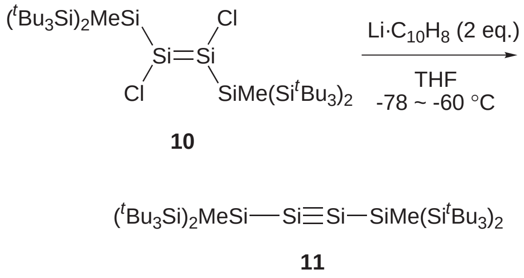


Scheme 2.

The compound **4** was synthesized as a possible precursor of dimethyldisilyne (**5**) by the retro-Diels–Alder reaction. When **4** was heated in the presence of anthracene at 350 °C, the anthracene adduct **6** of MeSi≡SiMe was produced together with 1,2,3,4-tetraphenylnaphthalene (Scheme 1). The anthracene adduct **6** is also a possible dimethyldisilyne precursor. In this connection, the mass spectrum of **6** (EI, 30 eV) is suggestive; peaks were observed at *m*/*z* 442 (M^+, relative intensity 35), 264 (M^+ − anthracene, 100), 249 (M^+ − anthracene − Me, 36), and 178 (anthracene$^+$, 50). In addition to these, a peak with a relative intensity of 15 was found at *m*/*z* 86. The exact mass and isotope ratios of this peak show that it has the molecular formula $C_2H_6Si_2{}^+$.

The synthesis of the silicon analogue of an alkyne having a terphenyl ligand has been attempted by West and co-workers.[14] Thus, the reductive coupling of 2,6-dimesitylphenyltrifluorosilane (**7**) with three equivalents of sodium in THF led to a product with the formal constitution $(Mes_2C_6H_3Si)_2$. However, the product is not a disilyne, but the bis(silafluorenyl) **8**. The disilyne **9** is postulated as an intermediate in this reaction (Scheme 2).

The closest work to a stable disilyne was reported by Wiberg et al. in 2002.[15] Thus, as shown in Scheme 3, the reaction of the disilene $({}^t\mathrm{Bu_3Si})_2\mathrm{MeSi(Cl)Si{=}Si(Cl)SiMe(Si}{}^t\mathrm{Bu_3})_2$ (**10**) with lithium naphthalenide in THF forms a reaction mixture containing a chlorine free species, which gives a low field ^{29}Si NMR signal at 91.5 ppm, which lies in the region that is reasonable for a triply-bonded silicon atom and is consistent enough with the calculated value for $({}^t\mathrm{Bu_3Si})_2\mathrm{MeSiSi{\equiv}SiSiMe(Si}{}^t\mathrm{Bu_3})_2$ (**11**) ($\delta_{\mathrm{Si{\equiv}Si}} = 111.2$ ppm).[16] The disilyne **11** is not stable enough in solution at room temperature to be isolated and full characterization had not been reported until now. However, very recently the trapping reactions of **11** with ethylene and 1,3-butadiene to give the corresponding cyclic disilenes have been reported (vide infra).[17]



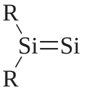
Scheme 3.

Although the theoretical analysis predicted the experimental accessibility of disilynes with a silicon–silicon triple bond,[16,18] all attempts to isolate such postulated molecules prior to our report had been unsuccessful. The difficulty in synthesizing disilynes is in part due to their high reactivitiy, especially toward dimerization and isomerization.[14,17,19,20]

2. Our Project to Synthesize a Stable Disilyne

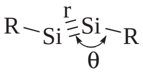
We started the project on the synthesis of a stable disilyne in 1998. First, we looked at which type of bulky substituent would be appropriate for the synthesis of a stable disilyne. Theoretical calculations not only on the parent H_2Si_2, but also on R_2Si_2 with various substituents R have been reported so far.[13] Among them, the calculation by Nagase et al. reported some very important predictions: the introduction of the electropositive silyl group on the triply-bonded Si atom, especially a triorganosilyl group, instead of hydrogen or organic groups, such as methyl, extensively reduces the energy difference between the *trans*-bent and linear forms with an increase in the bend angle in the *trans*-bent structure (the geometry of the *trans*-bent structure becoming much closer to linear) (Tables 1 and 2).[21] Furthermore, the disilavinylidene structure, which is the most stable isomer for R_2Si_2 except for the case of R = H, would be relatively destabilized by the introduction of more bulky substituents on the silicon atoms. Thus, it is highly likely that the introduction of ${}^tBu_3Si$ or Dep_3Si groups, or their derivatives, would reverse the relative stability between *trans*-bent disilyne and disilavinylidene, the *trans*-bent structure being favored over disilavinylidene.

Table 1. Relative Energies ($kcal\,mol^{-1}$) of the Linear Disilyne, *trans*-Bent Disilyne, and Disilavinylidene of R_2Si_2[a)]

R	$R{-}Si{\equiv}Si{-}R$[b)]		
H	0.0	−20.3 (−22.1)	−28.2 (−30.7)
Me	0.0	−18.4 (−20.4)	−25.3 (−28.2)
SiH_3	0.0	−10.1 (−12.1)	−15.7 (−17.7)
SiF_3	0.0	−13.3 (−15.8)	−30.1 (−25.6)
$SiMe_3$	0.0	−7.0 (−8.5)	−10.5 (−11.4)
$SiPh_3$	0.0	−7.2	−17.3
$Si(SiH_3)_3$	0.0	−10.4	−16.6
Si^tBu_3	0.0	−4.0	5.7
$SiDep_3$[c)]	0.0	−5.5	6.5

a) At B3LYP/3-21G(d) level (B3LYP/6-31G(d) level in parentheses, Ref. 21). b) Linear disilynes have two imaginary frequencies. c) Dep = $2,6\text{-}Et_2C_6H_3$.

Table 2. Structural Parameters of *trans*-Bent Disilyne[a)]

R	 ${}^rSi{\equiv}Si/Å$	${}^{\theta}Si{\equiv}Si{-}R/deg$
H	2.093 (2.111)	124.9 (124.4)
Me	2.104 (2.123)	129.2 (128.9)
SiH_3	2.082 (2.100)	130.0 (130.0)
SiF_3	2.069 (2.094)	128.8 (126.6)
$SiMe_3$	2.075 (2.095)	135.6 (131.3)
$SiPh_3$	2.078	133.5
$Si(SiH_3)_3$	2.092	128.4
Si^tBu_3	2.068	138.2
$SiDep_3$[b)]	2.072	141.0

a) At B3LYP/3-21G(d) level (B3LYP/6-31G(d) level in parentheses, Ref. 21). b) Dep = $2,6\text{-}Et_2C_6H_3$.

3. Design of a New Substituent for the Isolation of a Stable Disilyne

Based on both the theoretical prediction and experimental experience, we have designed bulky trialkylsilyl groups that have plural bis(trimethylsilyl)methyl (Dis) on the silicon atoms, such as Dis_3Si and $Dis_2(R)Si$ (R = Me, Et, ${}^iPr$, ${}^tBu$, etc.) groups as a protecting group. The preparation of Dis_3SiH by the reaction of Dis_2SiBrH with DisK, along with the subsequent transformation to Dis_3SiBr and Dis_3SiI, was finally achieved. However, we could not prepare the alkali metal derivative of Dis_3SiM (M = Li, Na, and K) as a key reagent for the introduction of the Dis_3Si group to the silicon atom.

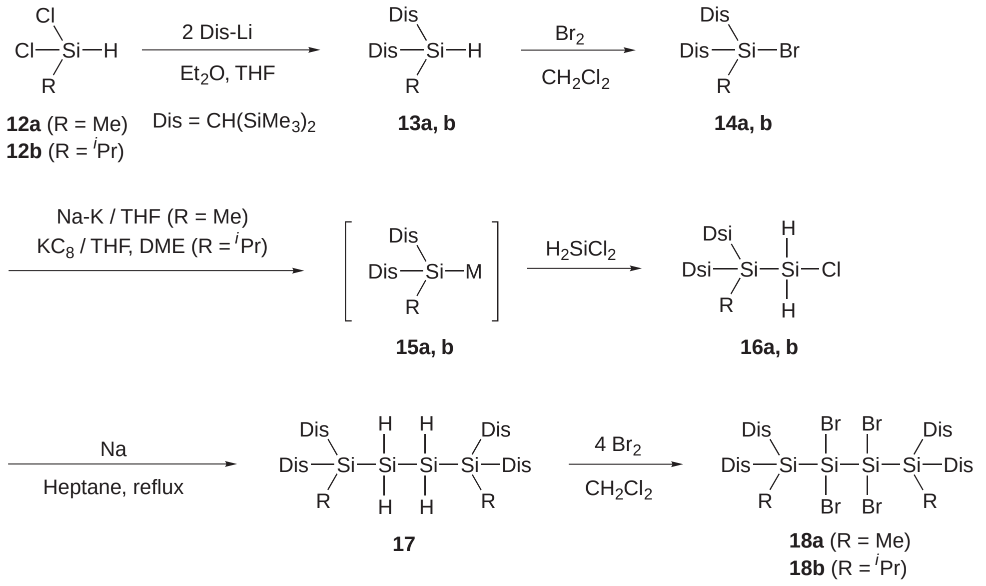
A second candidate of $Dis_2(R)Si$ (R = Me and ${}^iPr$) as a protecting group was prepared as the corresponding hydrosilanes by the reaction of $RSiCl_2H$ **12** with two equivalents of DisLi (Scheme 4). The following halogenation, metallation, and coupling reaction with H_2SiCl_2 afforded chlorodihydrosilane bearing one bulky Dis_2RSi group ($Dis_2RSi{-}SiH_2Cl$, **16**). Reductive coupling of **16** with molten sodium in heptane gave the tetrahydrodisilane derivative **17**, and the tetrabromide precursors **18** were easily obtained by bromination with four equivalents of bromine.

We initially investigated the reductive debromination of **18a** having the Dis_2MeSi group by using various reducing agents such as alkali metals (Li, Na, and K), lithium naphthalenide, potassium graphite, and finally revealed the formation of tetrasilatetrahedrane **19** by the reaction with ${}^tBu_3SiNa$ in 46% yield (Scheme 5).[20] This clearly indicates that the Dis_2MeSi group is not large enough to prevent the dimerization of the Si≡Si triple bond species. Next, we used the more bulky $Dis_2{}^iPrSi$ group for the synthesis of a stable disilyne.

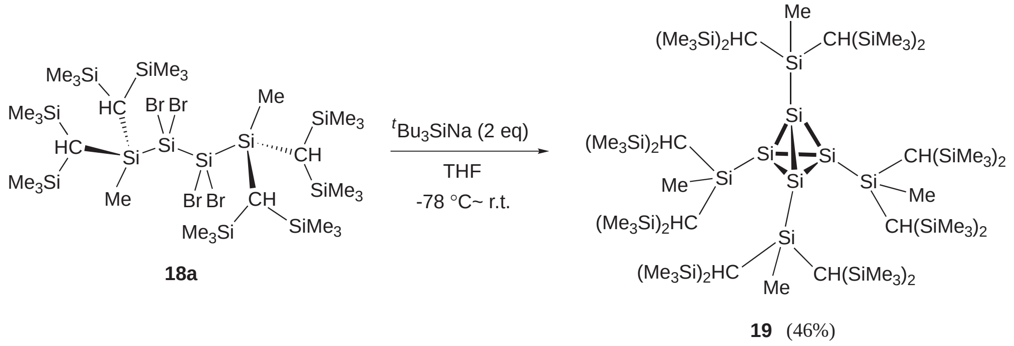
4. Synthesis and X-ray Crystal Structure of a Stable Disilyne

Finally, the first isolable disilyne **20** bearing $Dis_2{}^iPrSi$ groups was synthesized by the reductive debromination of the tetrabromodisilane precursor **18b** with four equivalents of potassium graphite (KC_8) in dry THF.[22] Despite the large steric congestion of **18b**, the reaction proceeded rapidly and cleanly. After removal of the resulting graphite and inorganic salts, recrystallization from pentane at −30 °C of the dark green residue gave **20** as extremely air- and moisture-sensitive emerald green crystals in 73% isolated yield (Scheme 6). The disilyne **20** is stable in the solid state and sufficiently stable to isolate even in solution at room temperature.

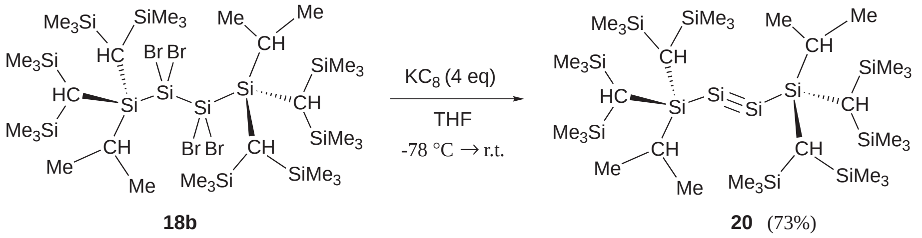
The molecular structure of the disilyne **20** was determined by X-ray crystallography (Fig. 3). The most important feature is the length of the Si1–Si1′ triple bond of 2.0622(9) Å. This value is 3.4% shorter than the shortest known Si=Si double bond (2.132 Å)[23] and 13.5% shorter than the average Si–Si single bond length of 2.34 Å. This shortening is half the magnitude of that in the carbon counterparts. Furthermore, alkynes have a linear geometry around the C≡C triple bond, whereas disilynes have been predicted to have a highly pronounced *trans*-bent geometry around the Si≡Si triple bond. The structure confirms this prediction: the four Si atoms (Si2, Si1,



Scheme 4.



Scheme 5.



Scheme 6.

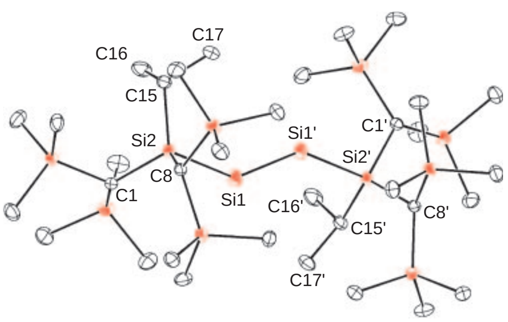
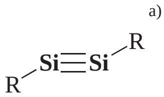
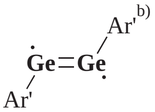
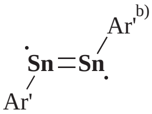
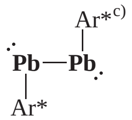


Fig. 3. ORTEP drawing of disilyne **20**. Hydrogen atoms are omitted for clarity.

Si1′, and Si2′) are coplanar and *trans*-bent with a bond angle of 137.44(4)°, as determined by the Si2–Si1–Si1′ angle. One methyl group of the isopropyl group (C17 and C17′) covers the triply-bonded silicon atom, and this is the reason that the disilyne **20** bearing $Dis_2{}^iPrSi$ groups could be isolated as a stable compound, but the Dis_2MeSi group could not suppress the dimerization of disilyne to form the tetrasilatetrahedrane derivative.[20]

The stable homonuclear alkyne analogues of all heavier group 14 elements have now been synthesized. The structural comparisons of R–E≡E–R (E = Si, Ge, S, and Pb) are summarized in Table 3. The strong *trans*-bending observed in these compounds shows that the bond order is less than three and

Table 3. Comparative Data of Heavier Analogues of the Alkynes E_2R_2 (E = Si, Ge, Sn, and Pb)

E_2R_2				
Color	Emerald Green[d)]	Orange Red[e)]	Purple[f)]	Dark Green[g)]
$d_{E\text{–}E}$/Å	2.0622(9)	2.2850(6)	2.6675(4)	3.1881(10)
$\theta_{E\text{–}E\text{–}R}$/deg	137.44(4)	126.67(8)	125.24(7)	94.26(4)

a) R = $Si^iPr[CH(SiMe_3)_2]_2$. b) Ar′ = 2,6-$Dep_2C_6H_3$. c) Ar* = 2,6-$Tip_2C_6H_3$. d) Ref. 22. e) Ref. 11. f) Ref. 10. g) Ref. 9.

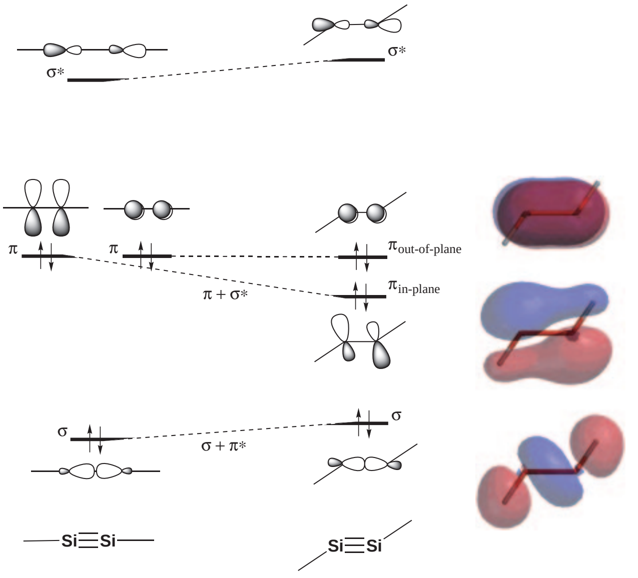


Fig. 4. Schematic MO diagram of linear and *trans*-bent disilynes.

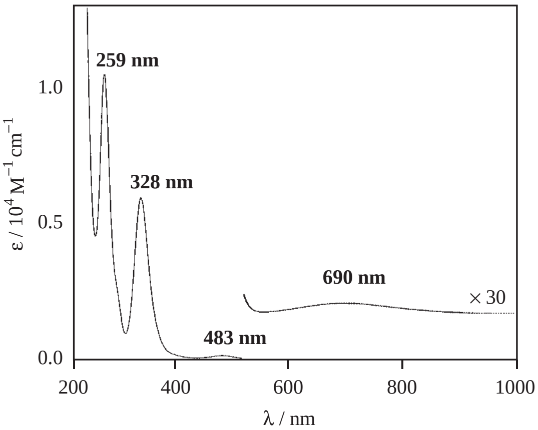


Fig. 5. UV–vis spectrum of disilyne **20** in hexane at room temperature.

that the non-bonding lone-pair character increases as group 14 is descended. The bending is thought to be the result of the mixing of an in-plane π-orbital with a σ^* orbital whose energies are close enough to cause the interaction of these orbitals in the heavier elements (Fig. 4). The σ orbital of the C–C bond cannot interact with an in-plane π-orbital because of the large energy difference, whereas the Si–Si σ^* orbital can interact with the in-plane π-orbital to produce the *trans*-bent structure of R*–Si≡Si–R* (R* = $Si^iPr[CH(SiMe_3)_2]_2$), resulting in the bond order of 2.618. However, Ar*PbPbAr* (Ar* = C_6H_2-2,4,6-$^iPr_3$) has Pb–Pb bonding that is essentially a single bond and there is a lone pair at each Pb atom.[7a] The Ge and Sn alkyne analogues lie between those of Si and Pb, with bond orders of 2.1.[7a]

5. Spectral Properties of Disilyne 20

The stable disilyne **20** was fully characterized by several spectroscopic techniques. The ^{1}H and ^{13}C NMR spectra of **20** indicate that only one kind of $Dis_2{}^iPrSi$ group is present in the molecule. In the ^{29}Si NMR spectra, four signals with equal intensity at −0.3, 0.0, 20.7, and 89.9 ppm were observed by using an inverse-gated pulse sequence. The first two signals at −0.3 and 0.0 ppm correspond to four $CH(SiMe_3)_2$ groups, the third one at 20.7 ppm corresponding to the silicon atom bonded to a triply-bonded silicon atom. The last signal at 89.9 ppm is assignable to triply-bonded silicon atoms. The resonance of the sp-hybridized silicon atoms is apparently shifted to a higher field when compared with that of silyl-substituted disilenes (142.1 to 154.5 ppm),[24] as was observed in the case of the ^{13}C NMR chemical shifts of silyl-substituted alkenes (188 to 197 ppm) and alkynes (112 to 114 ppm).[25] The mass spectrum shows a clear parent ion peak at $m/z = 834$, and reasonable fragmentation peaks for disilyne.

The UV–vis spectrum of **20** in hexane at room temperature shows two weak absorption peaks at 690 and 483 nm in the visible region and two relatively strong absorption peaks at 328 and 259 nm in the ultraviolet region (Fig. 5). A significant temperature dependence of the UV–vis spectrum of **20** was not observed at lower temperature.

6. A DFT Calculation on Disilyne 20

A DFT calculation on the disilyne **20** at the B3LYP/6-31G(d) level of theory well reproduces the experimental geometry and the structural parameters (calculated value: 2.093 Å for the Si≡Si bond length, 136.1° for the *trans*-bending angle). The molecular orbitals (MOs) of **20** calculated at the HF/6-311G(d)//B3LYP/6-31G(d) level are shown in Fig. 6. Because of the *trans*-bent geometry of **20**, each pair of π- and π^*-orbitals are not equivalent: the two non-degenerate highest occupied π-MOs (HOMO−1 and HOMO) and two lowest unoccupied antibonding π^*-MOs (LUMO and LUMO+1). The out-of-plane HOMO and LUMO+1 are represented by the pure (p_z–p_z) π-MOs, whereas the in-plane HOMO−1 and LUMO are represented mainly by (p_y–p_y) π-MOs with a slight contribution from the antibonding σ^*(Si–Si) orbital of the central bond. In accordance with the triple-bond structure, natural bond orbital analysis of **20** shows electron occupancy of the two π(Si–Si) orbitals (1.934 and 1.897 electrons), indicating their bonding character. The bond order (Wiberg bond index) of Si1–Si1′ is 2.618, which agrees with the real Si≡Si triple bond.

A time-dependent (TD) DFT calculation on **20** at the B3LYP/6-31G(d) level calculated three π–π^* transitions at 734.6 nm (HOMO → LUMO, f (oscillator strength) $= 0.0020$), 502.9 nm (HOMO−1 → LUMO/HOMO → LUMO+1, $f = 0.0086$), and 402.0 nm (HOMO−1 → LUMO+1, $f = 0.0016$). On the basis of the TD-DFT calculation, weak absorption peaks at 690 and 483 nm in the visible region could be assigned to HOMO → LUMO and HOMO−1 → LUMO/HOMO → LUMO+1, respectively. The shortest wavelength $\pi \rightarrow \pi^*$ transition of HOMO−1 → LUMO+1 is expected to be very weak, and may be overlapped by the tail of the strong absorption band at 328 nm involving the σ- and σ^*-orbitals of the tetrasilane skeleton.

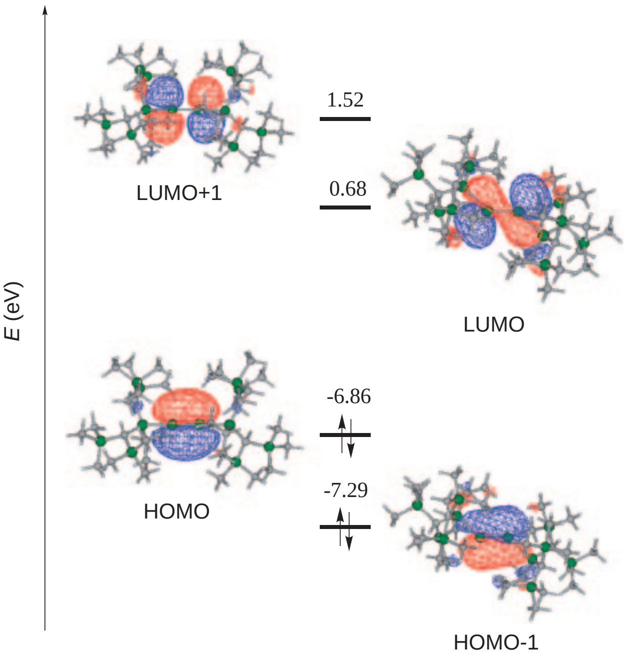


Fig. 6. Molecular orbitals of disilyne **20** calculated at the HF/6-311G(d)//B3LYP/6-31G(d) level.

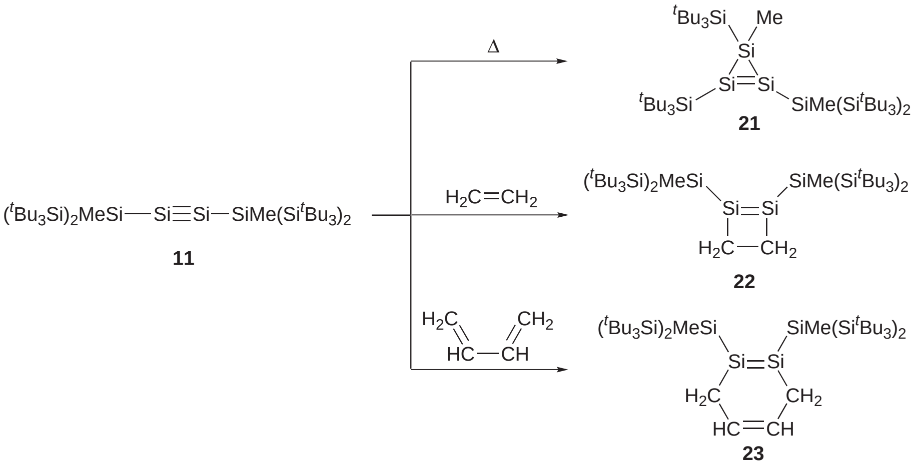
7. Reactivities of Disilynes

Some reactions of the $({}^t\mathrm{Bu_3Si})_2\mathrm{MeSi}$-substituted disilyne **11** generated by the reductive dehalogenation of the 1,2-dihalodisilane derivative **10** were very recently reported by Wiberg, and they are summarized in Scheme 7.[16] The disilyne **11** is not sufficiently stable in solution at room temperature and easily isomerizes to the cyclotrisilene **21** with the reorganization of one $({}^t\mathrm{Bu_3Si})_2\mathrm{MeSi}$ substituent. Reaction of **11** with ethylene and 1,3-butadiene afforded the corresponding [2 + 2]- and [4 + 2]-cycloaddition products **22** and **23** with a Si=Si double bond in the molecules, respectively.

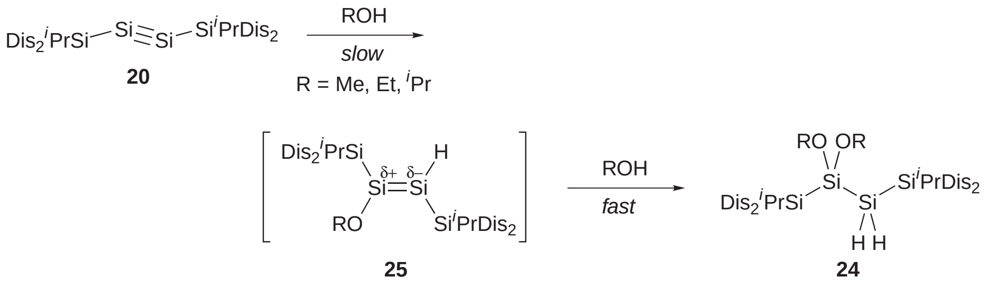
We have also started to study the reactivity of the disilyne **20**. Crystalline **20** is thermally stable up to 100 °C, but in solution, slow decomposition has been observed. At this time, it is not clear what type of reaction takes place in solution. The disilyne **20** is also slightly photolabile; irradiation of **20** in hexane solution with a light of wavelength longer than 420 nm caused slow decomposition, giving a complex mixture including a trace amount of $\mathrm{Dis_2{}^{i}PrSiH}$.

The addition of alcohols to the Si=Si double bond of disilenes is well known,[4] and we have investigated the reaction of **20** with various alcohols. The disilyne **20** reacted with an excess amount of MeOH, EtOH, and ^{i}PrOH to give 1,1-dialkoxydisilane derivatives $\mathrm{Dis_2{}^{i}PrSi{-}Si(OR)_2{-}SiH_2{-}Si{}^{i}PrDis_2}$ (**24**) in quantitative yield (Scheme 8).[26] On the other hand, ^{t}BuOH did not react, probably due to steric hindrance. When the mole ratio of **20** and alcohols was reduced to less than 1:2 (for example, 1:1), the 1:1 adduct $\mathrm{Dis_2{}^{i}PrSi(RO)Si{=}Si(H)\text{-}Si{}^{i}PrDis_2}$ (**25**) was not detected, and a mixture of **20** and **24** was obtained instead.

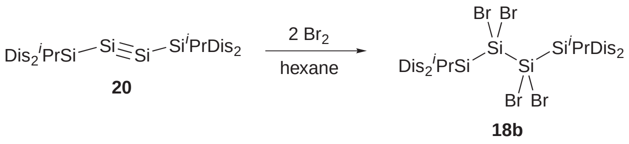
The Si=Si double bond of the intermediate **25** is polarized as shown in Scheme 8 due to the different electronic effect of the substituents (RO group and hydrogen). Therefore, the addition of the second alcohol molecule to the Si=Si double bond of **25** is regiospecific and faster than to the Si≡Si bond of **20** to



Scheme 7.



Scheme 8.



Scheme 9.

give **24** as the sole product. The Si$\equiv$Si triple bond in **20** also undergoes an addition reaction with a halogen (Scheme 9). The disilyne **20** readily reacted with two equivalents of bromine at room temperature in hexane to form **18b** in 94% isolated yield.

8. Conclusion and Outlook

In this account, we have summarized our recent results on isolable disilyne with a silicon–silicon triple bond utilizing an extremely bulky trialkylsilyl group. The molecular structure of the disilyne **20** with a short Si–Si bond length [2.0622(9) Å] and a *trans*-bent geometry [Si–Si$\equiv$Si bond angle: 137.44(4)°] has been determined by the X-ray crystallographic method. Our full characterization of a stable disilyne has been with the goal in mind of completing the heavier group 14 element alkyne analogue series as isolable compounds, which is also the starting point to the chemistry of disilynes. At this time, only one compound with a Si–Si triple bond has been isolated and fully characterized. The study of the reactivity of disilyne has just started, and the synthesis of a stable disilyne opens a new route to the multiple bond chemistry of the main group elements. The synthesis of other disilynes containing a variety of substituents and compounds with a triple bond between silicon and other elements, such as Si$\equiv$C and Si$\equiv$Ge, is the next challenge for the future.

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