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Unsymmetrically Substituted Disilyne $Dsi_2{}^iPrSi{-}Si{\equiv}Si{-}SiNpDsi_2$ ($Np = CH_2{}^tBu$): Synthesis and Characterization

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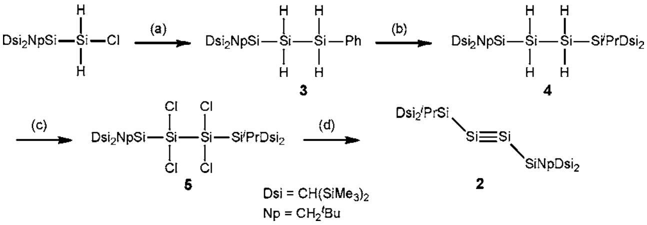
Abstract: The unsymmetrically substituted disilyne, $Dsi_2{}^iPrSi{-}Si{\equiv}Si{-}SiNpDsi_2$ ($Np = CH_2{}^tBu$) **2**, was synthesized and characterized by X-ray crystallography to show a *trans*-bent structure with a silicon−silicon triple bond length of 2.0569(12) Å. The ^{29}Si chemical shifts of the triply bonded silicon atoms of **2** are quite different, being observed at 62.6 ppm for the $Dsi_2{}^iPrSi$ side and 106.3 ppm for the Dsi_2NpSi side, indicating different hybridizations on the triply bonded silicon atoms at each site.

The chemistry of multiply bonded compounds containing heavier group 14 elements has been developed since the isolation of the stable distannene $Dsi_2Sn{=}SnDsi_2$ ($Dsi = CH(SiMe_3)_2$) by Lappert in 1973,[1] the tetramesityldisilene $Mes_2Si{=}SiMes_2$ (Mes = 2,4,6-trimethylphenyl), and the silene $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$ (Ad = 1-adamantyl) in 1981.[2−4] Despite extensive experimental efforts directed toward the synthesis of triply bonded compounds of heavier group 14 elements, heavier analogues of alkynes ($-E{\equiv}E-$; E = Si, Ge, Sn, and Pb) remained unknown until recently.[5] In 2000, Power reported the synthesis and structural characterization of a lead-alkyne analogue, ArPbPbAr ($Ar = 2,6\text{-}Tip_2C_6H_3$, $Tip = C_6H_2\text{-}2,4,6\text{-}{}^iPr_3$).[6] Subsequently, tin[7] and germanium[8] analogues were also synthesized by the same group in 2002 using bulky terphenyl ligands (2,6-diarylphenyl groups) and by Tokitoh's group using the Bbt substituent ($C_6H_2\text{-}2,6\text{-}[CH(SiMe_3)_2]_2\text{-}4\text{-}C(SiMe_3)_3$) for the germanium analogue.[9] Recently, this laboratory[10] and Wiberg et al.[11] independently succeeded in synthesizing silicon−silicon triply bonded species, disilynes, which in our case was isolated as emerald green crystals, $Dsi_2{}^iPrSi{-}Si{\equiv}Si{-}Si{}^iPrDsi_2$ (**1a**), and its *trans*-bent structure was unequivocally determined by X-ray crystallography as well as a solid-state ^{29}Si NMR study.[12] Later, Tokitoh's group reported an aryl-substituted disilyne by the use of very bulky aryl groups.[13] However, these heavy alkyne analogues have the same substituent on each skeletal atom, and no unsymmetrically substituted heavy alkynes, which will be important for elucidating the bonding nature of alkyne analogues, have been reported.[14] Herein, we report the synthesis and structure of the first isolable unsymmetrically substituted disilyne $Dsi_2{}^iPrSi{-}Si{\equiv}Si{-}SiNpDsi_2$ (**2**) ($Np = CH_2{}^tBu$), including its X-ray crystal structure, the unusual difference in the ^{29}Si chemical shifts of the triply bonded silicon atoms, theoretical calculations, and its thermal isomerization to a cyclotrisilene derivative.

To prepare the unsymmetrically substituted disilyne **2**, we have designed a stepwise method starting from $Dsi_2NpSiSiH_2Cl$, as depicted in Scheme 1.[15] Thus, the reaction of $Dsi_2NpSiSiH_2Cl$ with $Ph(R_2N)_2SiLi$ (R_2N = pyrrolidino) produced $Dsi_2NpSiSiH_2Si(NR_2)_2Ph$. Deaminative chlorination of $Dsi_2NpSiSiH_2Si(NR_2)_2Ph$ using HCl gas, followed by reaction with $LiAlH_4$, gave $Dsi_2NpSiSiH_2SiH_2Ph$ (**3**). The phenyl group of **3** was converted to the triflate by reaction with trifluoromethanesulfonic acid, giving silyltriflate, which was reacted with the silyl potassium $Dsi_2{}^iPrSiK$ to produce tetrahydrodisilane **4**.[16] Tetrachloro-precursor **5** for the unsymmetrically substituted disilyne was synthesized by the chlorination of **4** with 4 equiv of Cl_2 in CH_2Cl_2.[17] Finally, the reductive dechlorination of **5** using 4 equiv of KC_8 in THF gave the first stable unsymmetrically substituted disilyne, $Dsi_2{}^iPrSi{-}Si{\equiv}Si{-}SiNpDsi_2$ (**2**), as air- and moisture-sensitive emerald green crystals in 32% yield.[15]

Scheme 1. Synthesis of the Unsymmetrically Substituted Disilyne **2**[a]



[a] (a) (1) $Ph(R_2N)_2SiLi$ ($R_2N = (CH_2CH_2)_2N$), THF, 0 °C; (2) dry HCl, Et_2O, RT; (3) $LiAlH_4$, Et_2O, RT. (b) (1) CF_3SO_3H, toluene, RT; (2) $Dsi_2{}^iPrK$/HMPA/THF/DME, −50 °C. (c) Cl_2, CH_2Cl_2, −78 °C. (d) KC_8, THF, −78 °C.

The silicon−silicon triple bonds of all reported disilynes are *trans*-bent, not linear, which results in two nondegenerate occupied π-MOs (π_{in} as the HOMO − 1 and π_{out} as the HOMO) and two unoccupied antibonding π^*-MOs (π^*_{in} as the LUMO and π^*_{out} as the LUMO + 1).[10] The molecular structure of disilyne **2** as determined by X-ray crystallographic analysis is shown in Figure 1.[15] The disilyne **2** also exhibits a *trans*-bent structure with bending angles of 138.78(5)° for the $Dsi_2{}^iPrSi$ side and 137.89(5)° for the Dsi_2NpSi side. The $Si{\equiv}Si$ bond length of **2** (2.0569(12) Å) is remarkably shorter than typical $Si{=}Si$ bond lengths (2.143−2.228 Å),[18] demonstrating its triple-bond character, and is also shorter than those of **1a** (2.0622(9) Å)[10] and $Bbt{-}Si{\equiv}Si{-}Bbt$ (2.108(5) Å).[13] In the ^{29}Si NMR spectrum of **2** in C_6D_6, eight signals are observed at −3.5, −0.5, −0.3, 0.0, 0.1, 22.1, 62.6, and 106.3 ppm, the former six signals being due to the silicon atoms of the substituents. On the basis of 2-D Si−H NMR spectroscopy, the low magnetic field signal at 62.6 ppm can be assigned to the triply bonded silicon atom bearing the $Dsi_2{}^iPrSi$ group, and the other low magnetic field signal at 106.3 ppm can be assigned to the triply bonded silicon atom bearing the Dsi_2NpSi group (see Supporting Information). These ^{29}Si NMR resonances of the triply bonded silicon atoms in **2** are remarkably shifted to higher and lower fields compared with those of the corresponding symmetrically substituted disilynes (e.g., $Dsi_2{}^iPrSi$-substituted disilyne **1a**: 89.9 ppm, Dsi_2NpSi-substituted disilyne **1b**: 77.1 ppm).[10,15]

The structural parameters determined by X-ray crystallography are not fully explained by the different ^{29}Si chemical shifts of the

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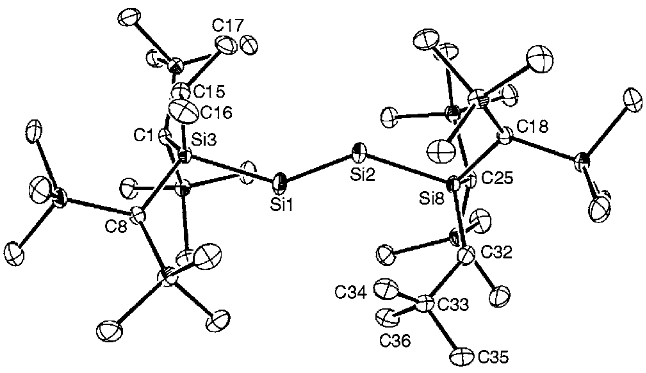


Figure 1. ORTEP drawing of **2** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1−Si2 = 2.0569(12), Si1−Si3 = 2.3598(11), Si2−Si8 = 2.3671(11), Si3−C1 = 1.901(3), Si3−C8 = 1.909(3), Si3−C15 = 1.920(3), Si8−C18 = 1.908(3), Si8−C25 = 1.907(3), Si8−C32 = 1.896(3). Selected bond angles (deg): Si3−Si1−Si2 = 138.78(5), Si1−Si2−Si8 = 137.89(5).

two triply bonded silicon atoms. Therefore, we have performed density functional theory (DFT) calculations on $Dsi_2{}^iPrSi{-}Si{\equiv}Si{-}SiNpDsi_2$ (**2**) at the GIAO/B3LYP/6-31G(d)//B3LYP/6-31G(d) level (see Supporting Information). The optimized structure of **2** shows a large bond angle difference between the two silicon termini; the $R{-}Si{\equiv}Si$ bond angles are 134.8° for the $Dsi_2{}^iPrSi$ side and 141.5° for the Dsi_2NpSi side, with a $Si{\equiv}Si$ bond length of 2.091 Å. The calculated ^{29}Si chemical shifts of the triply bonded silicon atoms of **2** were 87.6 ppm for the $Dsi_2{}^iPrSi$ side and 152.0 ppm for the Dsi_2NpSi side, supporting the experimental values of the different chemical shifts of the triply bonded silicon atoms.

Apeloig, Nagase et al. reported that small geometry changes in the $R{-}Si{\equiv}Si$ bond angle cause significant changes in the ^{29}Si chemical shifts of triply bonded silicon atoms.[19] To provide an estimate of the relationship between the ^{29}Si chemical shifts of triply bonded silicon atoms and the $R{-}Si{\equiv}Si$ bond angles, calculations were performed on the model compound $Me_3Si{-}Si^1{\equiv}Si^2{-}SiMe_3$ (**2′**). In these calculations, the bond angle of $Si{-}Si^2{\equiv}Si^1$ was fixed at 135° and θ ($Si{-}Si^1{\equiv}Si^2$) was the variable parameter, θ (θ = 90° to 180°). The potential energy curve for the bond angle of $Me_3Si{-}Si^1{\equiv}Si^2{-}SiMe_3$ is very flat (less than 1 kcal/mol) in the range from 120° to 150° (Figure 2a). Therefore, the difference in the bond angle of **2** between its X-ray structure and the optimized calculated structure is most probably due to crystal packing forces.[20] The calculated ^{29}Si chemical shifts of the two skeletal silicon atoms as a function of the bond angle θ are plotted in Figure 2b. As the bond angle θ increases, the calculated ^{29}Si values of Si^2 are significantly upfield shifted, from +100 (θ = 135°) to −25 ppm (θ = 180°), whereas the calculated ^{29}Si values of Si^1 are downfield shifted, from +100 (θ = 135°) to +200 ppm (θ = 180°). When the Si^1 atom has a larger bond angle than the Si^2 atom (when θ is larger than 135°), Si^1 is deshielded compared with Si^2, which supports the experimental values of the different ^{29}Si NMR chemical shifts of **2** (the Dsi_2NpSi side has a larger bond angle and is more deshielded than the $Dsi_2{}^iPrSi$ side). Based on the calculations in Figure 2b, we attribute the different ^{29}Si chemical shifts of the two triply bonded silicon atoms to the different $R{-}Si{\equiv}Si$ bond angles at each terminus. A more acute $R{-}Si{\equiv}Si$ bond angle causes a higher degree of 3s contribution to the in-plane π-orbital and as a result a higher field ^{29}Si NMR chemical shift (i.e., of the $Dsi_2{}^iPrSi{-}Si^*{\equiv}Si$ part).

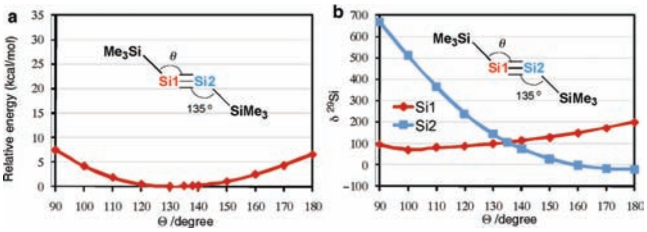
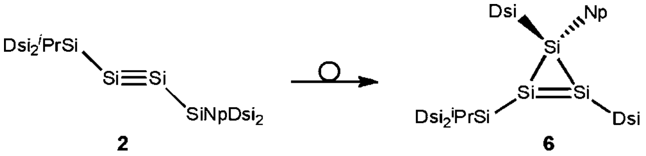


Figure 2. Theoretical calculations on $Me_3Si{-}Si^1{\equiv}Si^2{-}SiMe_3$ **2′** (the bond angle of $Si{-}Si^2{\equiv}Si^1$ is fixed at 135° and θ ($Si{-}Si^1{\equiv}Si^2$) is the variable parameter): (a) relative energies and (b) chemical shifts of skeletal silicon atoms (red line for Si^1 and blue line for Si^2) calculated at the GIAO/B3LYP/6-311G(d)//6-31G(d) level.

Scheme 2. Isomerization of the Disilyne **2** to Cyclotrisilene **6**



The unsymmetrically substituted disilyne **2** slowly underwent isomerization in solution at room temperature, giving cyclotrisilene derivative **6** as the sole product (Scheme 2).[21] Although the mechanism for the formation of cyclotrisilene **6** by the thermal reaction of **2** is uncertain, we can suggest that the reaction pathway would involve two steps: migration of the Dsi group followed by cyclization of the $Si{-}Si{\equiv}Si$ unit. Interestingly, the rearrangement and cyclization occurred only on the Dsi_2NpSi side to produce **6** as the sole product, probably for steric reasons.

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Supporting Information Available: The experimental procedures and spectral data for new compounds in Scheme 1, **1b**, and **6**, computational results for the compound **2** and the model compound **2′**, tables of crystallographic data, including atomic positional and thermal parameters for **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) For the experimental procedures and spectral data for new compounds in Scheme 1, a disilyne **1b**, and **6** and crystal data for **2**, see the Supporting Information.

(16) The Dsi_2NpSi group is large enough to protect the active triply bonded silicon part against dimerization and isomerization. Disilyne $Dsi_2NpSi{-}Si{\equiv}Si{-}SiNpDsi_2$ (**1b**) was synthesized by the reductive debromination of the corresponding tetrabromo-precursor (see Supporting Information).

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(21) Isomerization of a disilyne to a cyclotrisilene derivative was reported for Wiberg's disilyne. See ref 11.

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