Theoretical Study of an Isolable Compound with a Short Silicon-Silicon Triple Bond, $(tBu_3Si)_2MeSiSi{\equiv}SiSiMe(SitBu_3)_2$

Nozomi Takagi[a] **and Shigeru Nagase***[a]

Keywords: Silicon / Multiple bonds / Substituent effects / Density functional calculations

The effects of a very bulky silyl group [R**, -SiMe(Si-tBu$_3$)$_2$] — developed recently by Wiberg and co-workers — on silicon-silicon triple bonding have been investigated by density functional theory in search of a stable disilyne. These calculations predict that R**Si≡SiR** is stable enough to be isolated and has a short Si-Si bond length of 2.072 Å that is short enough to be a triple bond.

Introduction

Since the first isolation of a stable disilene ($R_2Si{=}SiR_2$) in 1981,[1] a variety of synthetic methods have been developed for the synthesis of silicon-silicon doubly bonded compounds, as summarized in recent reviews.[2-4] However, stable silicon-silicon triply bonded compounds [disilynes (RSi≡SiR)] are still unknown, despite several attempts to isolate them,[5] except for their transient existence as intermediates.[6,7] It is the focus of much current interest whether disilynes are synthetically accessible and isolable as stable compounds.[3,4,8,9] The major difficulty in synthesizing and isolating disilynes is due to their high reactivities, especially toward isomerization and dimerization.[10-14] To suppress these reactivities, substituent effects have been extensively investigated.[10-14] Bulky aryl groups such as Tbt [C_6H_2-2,4,6-$\{CH(SiMe_3)_2\}_3$] and Ar* [C_6H_3-2,6-(C_6H_2-2,4,6-iPr$_3$)$_2$][15] have been suggested as sterically promising substituents.[12,13]

According to theoretical investigations,[10,11] substitution by electropositive silyl groups is electronically much more effective in realizing a less trans-bent disilyne structure with a short silicon-silicon multiple bond. Thus, silyl groups such as SitBu$_3$ and SiDep$_3$ (Dep = 2,6-diethylphenyl) have been tested as bulky candidates.[10,11] However, it has been found that they are not sufficiently bulky to make disilynes isolable under normal conditions.[12,16] Therefore, the availability of much bulkier silyl groups has been anticipated. In this context, it is worthy to note that Wiberg and co-workers have very recently developed the extremely bulky silyl group R** [SiMe(SitBu$_3$)$_2$] and succeeded in synthesizing and isolating a stable 1,2-dichlorodisilene, R**ClSi=SiClR**, with the R** groups in trans positions, as reported in this journal.[17] It has been suggested that dechlorination of R**ClSi=SiClR** could lead to an isolable disilyne, R**Si≡SiR**. To confirm this interesting suggestion, we have performed theoretical calculations on R**Si≡SiR**.

Results and Discussion

Hybrid density functional calculations at the B3LYP level[18] were performed with the 3-21G* basis set,[19] as in a series of previous studies,[10-14] using the Gaussian 98 program.[20] Since the structure of R**ClSi=SiClR** has been determined by X-ray crystal analysis,[17] its geometry optimization was first carried out to calibrate the B3LYP/3-21G* calculations. As found for the X-ray crystal structure, it was calculated that R**ClSi=SiClR** has a planar structure around the Si-Si double bond with C_i symmetry. The calculated bond lengths and angles were R**-Si = 2.397 Å, Cl−Si = 2.116 Å, R**-Si-Si = 135.9°, and Cl−Si−Si = 108.0°. These values agree very well with the X-ray crystal data of R**-Si = 2.401 Å, Cl−Si = 2.091 Å, R**-Si-Si = 132.0°, and Cl−Si−Si = 106.8°. The Si-Si double bond length was calculated to be 2.171 Å, this being only 0.008 Å longer than the X-ray crystal structure value of 2.163 Å.

The optimized structure of R**Si≡SiR** is shown in Figure 1; it has C_2 symmetry. Owing to the two bulky R** groups, the skeleton of R**Si≡SiR** is only twisted around the central Si-Si bond by 1.0°, as shown by the dihedral R**-Si-Si-R** angle (ω) of 179.0°. However, the two bulky R** groups help to protect the central Si-Si bond from the attack of reactive reagents (see Figure 1). Silicon has a low tendency to form an ideal hybrid orbital because of the size difference between valence s and p orbitals.[10,11,21] For this reason, it is normal that disilynes prefer a highly trans-bent structure with some lone pair character at each Si atom, in contrast to the well-known linear

---

[a] Department of Theoretical Studies, Institute for Molecular Science,
Okazaki 444-8585, Japan
E-mail: nagase@ims.ac.jp

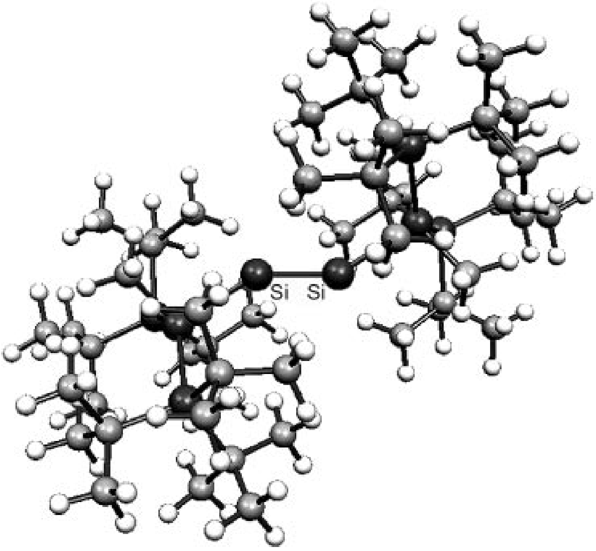

Figure 1. Optimized structure of R**Si≡SiR**; Si-Si = 2.072 Å and R**-Si-Si = 148.0°

structure of the carbon analogues. For R**Si≡SiR**, the R**-Si-Si bond angle (θ) was calculated to be 148.0°. It is noticeable that the trans-bending is 23.1° smaller than that for HSi≡SiH (θ = 124.9°). In addition, the energy difference between trans-bent and linear structures is only 5.5 kcal/mol for R**Si≡SiR**, while it is 20.3 kcal/mol for HSi≡SiH.

More interesting is the central Si-Si bond length of 2.072 Å calculated for R**Si≡SiR**, which is shorter than that of 2.093 Å for HSi≡SiH and considerably shorter than those of 2.121 and 2.136 Å calculated at the same level of theory for TbtSi≡SiTbt (θ = 130.9° and ω = 180.0°)[12] and Ar*Si≡SiAr* (θ = 129.0° and ω = 171.2°),[13b] owing to the much less trans-bent structure. The advantage of the R** group in the Si-Si bond shortening and skeletal linearization for R**Si≡SiR** is due to the fact that the SiR** components have a very small doublet-quadruplet energy difference of 28.5 kcal/mol because of the electropositive character of R**, as compared with the values of 42.6, 50.1, and 55.1 kcal/mol for SiH, SiTbt, and SiAr*, respectively; for the importance of the small doublet-quadruplet energy gap, see refs.[10,11]

The Si-Si bond length of 2.072 Å for R**Si≡SiR** is 0.1 Å shorter than the Si-Si double bond length of R**ClSi=SiClR** and 0.13−0.18 Å shorter than those of 2.202−2.251 Å determined for tetrasilyldisilenes R$_2$Si=SiR$_2$ (R = SiMe$_2t$Bu, SiMeiPr$_2$, and SiiPr$_3$).[22] These results clearly suggest that R**Si≡SiR** possesses an additional bond between the Si atoms, as compared with disilenes; it is interesting that the Si-Si distance is very close to an "idealized" Si-Si triple bond length of 2.025 Å in the linear structure of R**Si≡SiR**.[23] In an attempt to reduce the crowding of the substituents, the Me group in R** [SiMe(SitBu$_3$)$_2$] was replaced by an H atom. After this replacement the Si-Si distance increased to 2.081 Å, and the trans-bending and twisting were enhanced by 4.6 and 6.1°, respectively, thus showing that even the small Me group in R** plays an important role.[24]

The bulk of the R** group helps to destabilize the 1,2-R**-shifted isomer SiSiR**R**, because the two R** groups crowd more around one end of the Si-Si bond, as is apparent from Figure 2. Thus, R**Si≡SiR** was calculated to be 33.4 kcal/mol more stable than SiSiR**R**. This energy difference is large enough to prevent the 1,2-R** shift in R**Si≡SiR**. The corresponding energy differences are 18.5 and 37.9 kcal/mol for TbtSi≡SiTbt[12] and Ar*Si≡SiAr*,[13b] while they are only 9.8 and 12.0 kcal/mol for tBu$_3$SiSi≡SiSitBu$_3$ [10] and Dep$_3$SiSi≡SiSiDep$_3$,[10] respectively.

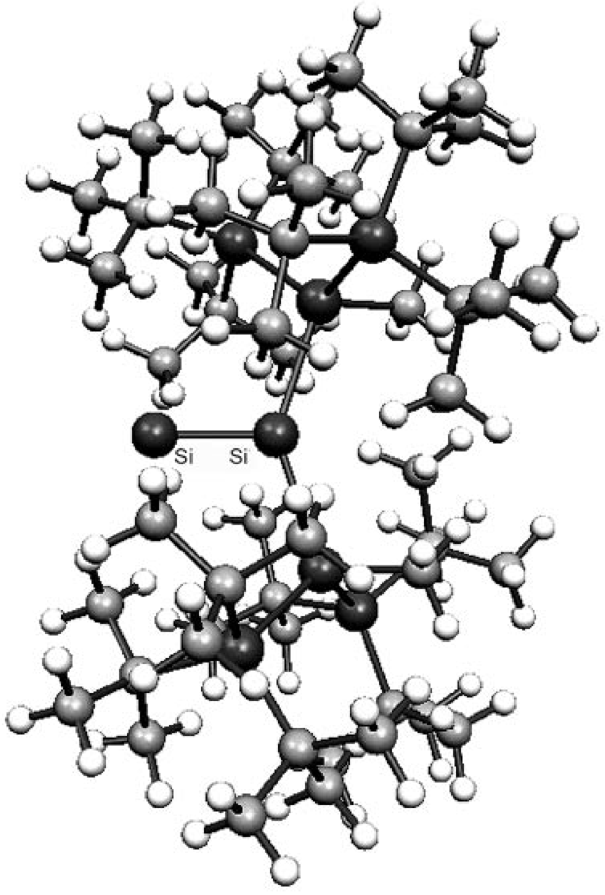

Figure 2. Optimized structure of the SiSiR**R** isomer; Si-Si = 2.187 Å and R**-Si-R** = 143.9°

Because of the bulk of the R** group, it may be argued that R**Si≡SiR** dissociates readily in solution. However, the energy required to cleave the central Si-Si bond (leading to two SiR** fragments in the doublet ground-state) was calculated to be 55.1 kcal/mol, this value being larger than those of 51.8 and 37.9 kcal/mol calculated for TbtSi≡SiTbt[12] and Ar*Si≡SiAr*,[13b] respectively. The dissociation energy of R**Si≡SiR** is 20.3 kcal/mol larger than the value of 34.8 kcal/mol calculated for R**ClSi=SiClR** (leading to two SiClR** fragments in the singlet ground-state), confirming that the two central Si atoms are strongly bonded in R**Si≡SiR**. According to orbital analysis, the

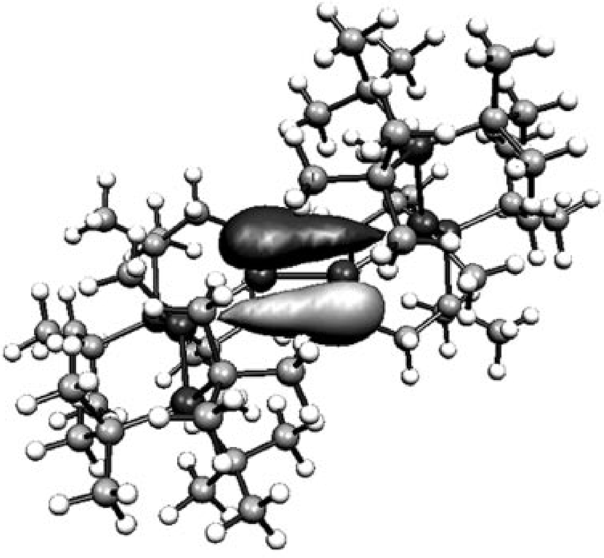

Figure 3. The Si-Si π-bonding orbital in the R*-Si-Si-R* plane of R**Si≡SiR** plotted with a value of 0.05 au

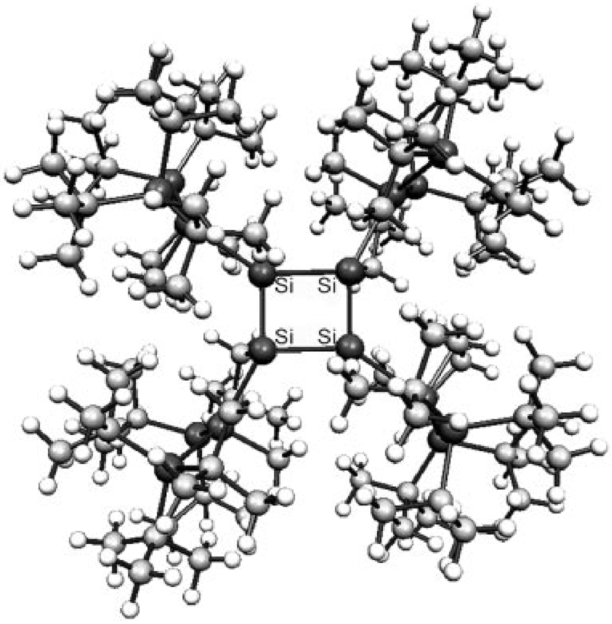

Figure 4. Optimized tetrasilabutadiene structure of the R**Si≡SiR** dimer; Si−Si = 2.227−2.534 Å and Si−Si−Si = 88.7−91.0°

Si≡Si bonding consists of a slightly distorted σ-bond, an out-of-plane π-bond, and a slipped in-plane π-bond due to the σ* mixing.[23] There has been much debate on the bonding contribution of a slipped π-bond.[3,5,8] As Figure 3 shows, however, the slipped in-plane π-orbital of R**Si≡SiR** has considerable bonding character between the Si atoms and helps to form a strong triple bond, though it is localized on each Si atom and becomes nonbonding as the trans-bending increases.

The most important obstacle to the isolation of disilynes is their facile dimerization to form tetrasilatetrahedrane or more stable tetrasilacyclobutadiene structures. To investigate to what extent R**Si≡SiR** is stable towards dimerization, calculations were carried out for a dimer of large size (a total of 1660 basis functions at the B3LYP/3-21G* level). Up to now, it has been predicted that the dimerization of $t\mathrm{Bu_3SiSi{\equiv}SiSi}t\mathrm{Bu_3}$ [12] and $\mathrm{Dep_3SiSi{\equiv}SiSiDep_3}$ [16] to form tetrasilatetrahedrane structures is exothermic by 80 and 32 kcal/mol, respectively. In this context, it is interesting to note that a stable tetrasilatetrahedrane has been synthesized using a reaction that involves most probably $t\mathrm{Bu_3SiSi{\equiv}SiSi}t\mathrm{Bu_3}$ as a transient intermediate.[25] In contrast, the dimerization of R**Si≡SiR** to a tetrasilacyclobutadiene structure (Figure 4) was calculated to be endothermic by 49.9 kcal/mol owing to the steric congestion of four bulkier R** groups. This large endothermicity confirms that R**Si≡SiR** is highly unlikely to dimerize.

In conclusion, R**Si≡SiR** is very stable towards both isomerization and dimerization. In addition, it has the least trans-bent structure and the shortest triple bond among isolable silicon analogues of alkynes that have ever been investigated.[10−14] It is expected that R**Si≡SiR** will soon be successfully isolated[26] and open up a new area in silicon chemistry.

Acknowledgments

This work was supported in part by a Grand-in-Aid from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

---

[1] R. West, M. J. Fink, J. Michl, *Science* **1981**, *214*, 1343−1344.
[2] R. Okazaki, R. West, *Adv. Organomet. Chem.* **1996**, *39*, 231−273.
[3] P. P. Power, *Chem. Rev.* **1999**, *99*, 3463−3503; P. P. Power, *J. Chem. Soc., Dalton Trans.* **1998**, 2939−2951.
[4] M. Weidenbruch, *Eur. J. Inorg. Chem.* **1999**, 373−381; M. Weidenbruch, *J. Organomet. Chem.* **2002**, *646*, 39−52.
[5] For a recent discussion on a Ga-Ga bond length as short as triple bonds, see: G. H. Robinson, *Acc. Chem. Res.* **1999**, *32*, 773−782; N. Takagi, M. W. Schmidt, S. Nagase, *Organometallics* **2001**, *20*, 1646−1651.
[6] A. Sekiguchi, S. S. Zigler, R. West, *J. Am. Chem. Soc.* **1986**, *108*, 4241−4242.
[7] R. Pietschnig, R. West, D. R. Powell, *Organometallics* **2000**, *19*, 2724−2729.
[8] K. W. Klinkhammer, *Angew. Chem.* **1997**, *109*, 2414−2416; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2320−2322.
[9] P. Jutzi, *Angew. Chem.* **2000**, *112*, 3953−3957; *Angew. Chem. Int. Ed.* **2000**, *39*, 3797−3800.
[10] K. Kobayashi, S. Nagase, *Organometallics* **1997**, *16*, 2489−2491.
[11] S. Nagase, K. Kobayashi, N. Takagi, *J. Organomet. Chem.* **2000**, *611*, 264−271.
[12] K. Kobayashi, N. Takagi, S. Nagase, *Organometallics* **2001**, *20*, 234−236.
[13] [13a] N. Takagi, S. Nagase, *Chem. Lett.* **2001**, 966−967. [13b] It has recently been found that the structure with the central aryl rings of the terphenyl groups (Ar*) nearly coplanar to the Si≡Si part is 6.2 kcal/mol more stable than the somewhat more twisted structure (Si-Si = 2.126 Å, θ = 130.5 °, and ω = 163.9°) with the central aryl rings perpendicular to Si≡Si.[13a] This trend has also been found for Ar*Ge≡GeAr* and Ar*Sn≡SnAr* (to be published).
[14] N. Takagi, S. Nagase, *Organometallics* **2001**, *20*, 5498−5500.

[15] For recent reviews on the stabilization and synthesis of doubly bonded compounds using the Tbt and Ar* groups, see: B. Twamley, S. T. Haubrich, P. P. Power, *Adv. Organomet. Chem.* **1999**, *44*, 1−65; J. A. C. Clyburne, N. McMullen, *Coord. Chem. Rev.* **2000**, *210*, 73−99; R. Okazaki, N. Tokitoh, *Acc. Chem. Res.* **2000**, *33*, 625−630; T. Sasamori, Y. Arai, N. Takeda, R. Okazaki, Y. Fuyukawa, M. Kimura, S. Nagase, N. Tokitoh, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1−15. For the synthesis and isolation of silabenzene, see: K. Wakita, N. Tokitoh, R. Okazaki, S. Nagase, *Angew. Chem.* **2000**, *112*, 648−650; *Angew. Chem. Int. Ed.* **2000**, *39*, 634−636; K. Wakita, N. Tokitoh, R. Okazaki, N. Takagi, S. Nagase, *J. Am. Chem. Soc.* **2000**, *122*, 5648−5649.

[16] K. Kobayashi, S. Nagase, to be published.

[17] N. Wiberg, W. Niedermayer, G. Fischer, H. Nöth, M. Suter, *Eur. J. Inorg. Chem.* **2002**, 1066−1070.

[18] A. D. Becke, *Phys. Rev.* **1988**, *A38*, 3098−3100; A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5652; C. Lee, W. Yang, R. G. Parr, *Phys. Rev.* **1988**, *B37*, 785−789.

[19] W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. DeFrees, J. A. Pople, J. S. Binkley, *J. Am. Chem. Soc.* **1982**, *104*, 5039−5048.

[20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian 98, Gaussian, Inc., Pittsburgh, PA, **1998**.

[21] W. Kutzelnigg, *Angew. Chem.* **1984**, *96*, 262−286; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 272−295.

[22] M. Kira, T. Maruyama, C. Kabuto, K. Ebata, H. Sakurai, *Angew. Chem.* **1994**, *106*, 1575−1577; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1489−1491.

[23] Upon the trans-bending, the low-lying vacant σ*-orbital is mixed into the in-plane π-orbital (a second-order Jahn−Teller effect); this orbital mixing contributes to stabilization but makes the π-bond slipped and weakened.

[24] For the possible intermediate formation of RSi≡SiR [R = SiH(Si*t*Bu$_3$)$_2$], see: N. Wiberg, W. Niedermayer, H. Nöth, M. Warchhold, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1717−1722.

[25] N. Wiberg, C. M. M. Finger, K. Polborn, *Angew. Chem.* **1993**, *105*, 1140−1142; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1054−1056; N. Wiberg, *Coord. Chem. Rev.* **1997**, *163*, 217−252.

[26] It has been reported that the reduction of R**ClSi=SiClR** with LiC$_{10}$H$_8$ in THF leads to a reaction mixture containing a Cl-free product that shows a low field ^{29}Si NMR signal at δ = 91.5 ppm.[17] In an attempt to estimate ^{29}Si NMR chemical shifts of triply bonded Si atoms, GIAO-B3LYP calculations were carried out using B3LYP/3-21G* optimized structures; a larger 6-311G(3d) basis set was employed only for Si because of the size of molecules. At this level, the ^{29}Si NMR chemical shifts of H$_3$SiSi≡SiSiH$_3$ and MeSi≡SiMe were calculated at δ = 95.0 and 26.9 ppm, respectively. It may be informative that the ^{29}Si NMR chemical shift at δ = 111.2 ppm calculated for R**Si≡SiR** is much closer to the observed signal than that at δ = 180.4 ppm calculated for R**ClSi=SiClR**.

Received May 22, 2002
[I02264]