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Triple bonds between heavier Group 14 elements. A theoretical approach

Shigeru Nagase *, Kaoru Kobayashi, Nozomi Takagi

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo192-0397, Japan

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Dedicated to Professor P.v.R. Schleyer on the occasion of his 70th birthday

Abstract

By providing theoretical insight into the nature of triple bonding between heavier Group 14 elements, the electronic and steric effects of substituents on silicon–silicon triple bonds are investigated to make disilynes synthetically accessible as stable compounds. Synthetic targets worthy of experimental testing are predicted for RSi≡SiR. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Triple bonds; Heavier Group 14 elements; Substituent effects; Disilyne; Theoretical study

1. Introduction

Carbon–carbon double and triple bonds have played an important role in many fields of chemistry. For many years, the synthesis of double and triple bonds between heavier Group 14 elements has attracted special interest in main group chemistry [1]. Since the first isolation of a stable disilene ($R_2Si{=}SiR_2$) in 1981 [2], a variety of synthetic methods have been developed for the silicon and germanium analogues of alkenes [1,3]. Recent important progress has been marked by the synthesis of still heavier tin and lead analogues [4]. According to X-ray crystallographic data, the structures of $R_2M = MR_2$ (M = Si, Ge, Sn, and Pb) are generally not planar but *trans*-bent: as M becomes heavier, the degree of *trans*-bending is increasingly enhanced and the M–M distance becomes only marginally shorter or even longer than the corresponding single bonds. Following the synthesis of cyclotrigermenes in 1995 [5], Si–Si [6] and Sn–Sn [7] double bonds incorporated in a three-membered ring were also successfully synthesized last year. Meanwhile, it has been shown that a *cis*-bent Ge–Ge doubly bonded structure can even be realized for asymmetrically substituted cyclotrigermenes [8]. As isolable silaaromatic compounds, silabenzene [9] and 2-silanaphthalene [10] have been synthesized by protecting the reactive silicon center with bulky substituent groups.

In contrast to the remarkable progress in doubly bonded compounds, no stable compound featuring triple bonding between heavier Group 14 elements is known up to now [11] despite great interest [1,12]. Thus, it has been theoretically investigated whether the heavier analogues of alkynes are synthetically accessible and isolated in a stable form, by providing insight into the nature of triple bonding.

2. Results and discussion

2.1. The difference between carbon and its heavier homologues

For the parent disilyne (HSi≡SiH), it has been repeatedly calculated that its linear structure (**1**) does not correspond to an energy minimum on the potential energy surface but collapses to a *trans*-bent structure (**2**) which undergoes facile isomerization to more stable 1,2-H shifted (**3**) or dibridged (**4**) structures [13] (Chart 1).

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* Corresponding author. Tel.: +81-426-772554, fax: +81-426-772525.

E-mail address: nagase@snl70.chem.metro-u.ac.jp (S. Nagase).

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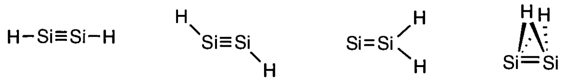

1 **2** **3** **4**

Chart 1

This trend is in sharp contrast to the carbon case: the linear structure of HC≡CH is a global minimum, while the bridge and 1,2-H shifted structures are highly unstable or not minima [14].

It is important to have an insight into the origin of the remarkable difference between the carbon and silicon cases. In this context, it is very helpful to consider the sizes of valence *n*s and *n*p atomic orbitals, since these orbitals play a central role in chemical bonding [15,16]. The atomic radii (r_{max}) of maximal electron density [17] are shown in Fig. 1. Upon going from C to Si, both the sizes of the *n*s and *n*p orbitals increase. This is not surprising since the principal quantum number increases from $n = 2$ to 3. Carbon has no occupied *p* orbital in the inner shell. However, silicon has occupied 2p orbitals in the inner shell. Therefore, the outer valence 3p orbitals are more diffuse than the corresponding 3s orbital because of exchange repulsion from the inner 2p orbitals (i.e. the orthogonality of the 3p and 2p orbitals).

As Fig. 1 shows, the sizes of valence *n*s and *n*p orbitals increase irregularly upon going from Si to Ge, Sn, and Pb. The irregularity at Ge is due to the fact that the d subshell is for the first time filled up but the shielding by d electrons is relatively small, as known in terms of d-block contraction [18]. The irregularity at Pb is due to the so-called relativistic effect. The heavier atom has a larger positive nuclear charge. Inner 1s electrons with no angular momentum can approach the atomic nucleus most closely, thereby their speed becoming close to the speed of light. As a result of mass–velocity correction [18], the inner 1s orbital shrinks. This orbital does not directly make an important contribution to chemical bonding. However, the shrinking of the 1s orbital causes the contraction and stabilization of the valence *n*s orbital. This is a reason why the size of the valence *n*s orbital decreases upon going from Sn to Pb, despite increasing *n*. The relativistic effect on the valence p orbitals is smaller since the angular momentum keeps p electrons away from the nucleus.

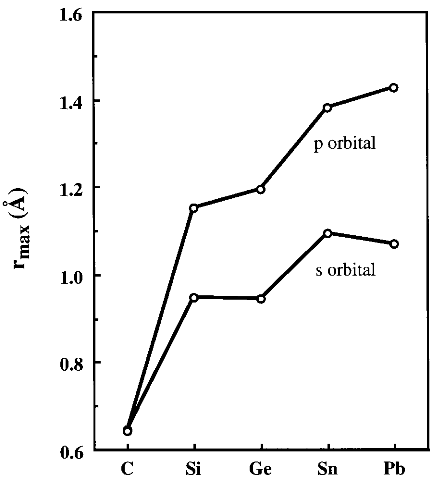

Fig. 1. The sizes of the valence s and p orbitals of Group 14 atoms.

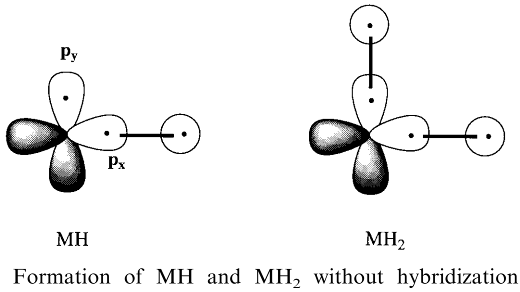

Fig. 2. Formation of MH and MH_2 without hybridization. For simplicity, the doubly occupied *n*s and vacant np_z (perpendicular to the plane) orbitals on M are omitted.

As is obvious from Fig. 1, carbon is special since it has almost equally sized valence s and p orbitals owing to the absence of inner p electrons. However, the sizes of the valence s and p atomic orbitals increase in a zigzag way and differ considerably for the heavier atoms. Therefore, the heavier atoms have a lower tendency to form 'good' hybrid orbitals [15], and they tend to preserve the valence *n*s electrons as core-like electrons in their compounds. In contrast, carbon prefers to make the 2s orbital singly occupied in order to take advantage of the strong overlap binding ability.

2.2. Bonding pattern

Because of the size difference, the heavier Group 14 atoms with valence $(ns)^2(np_x)^1(np_y)^1$ configuration prefer to form MH or MH_2 using the singly occupied *n*p atomic orbitals directly without hybridization, as shown in Fig. 2. Thus, MH_2 has a bond angle close to 90°. Since two electrons remain to be singlet paired in the *n*s orbital as a lone (or in some cases even an 'inert') pair, MH and MH_2 have doublet and singlet ground states, respectively. As M becomes heavier these trends are increasingly enhanced. This differs greatly from the fact that CH has a low-lying quartet state and the ground state of CH_2 is triplet with a larger bond angle of 136°.

These differences are explained as follows. Let us assume that CH and CH_2 are also formed, as shown in Fig. 2. The 2s orbital on C differs little in size from the 2p orbitals. Therefore, the 2s orbital interacts strongly with the C–H bonds formed to cause a mixing of 2s and 2p orbitals, i.e. hybridization on C (Chart 2). Because

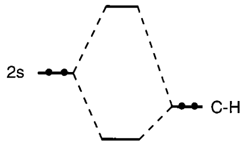

Chart 2.

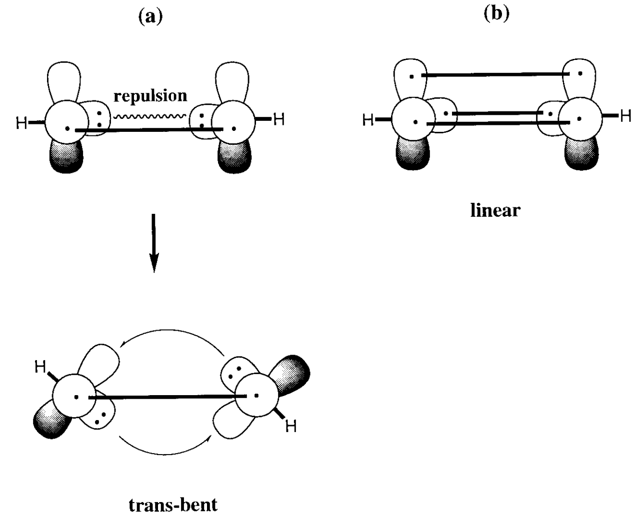

Fig. 3. Two interaction modes between MH. (a) Doublet–doublet coupling. (b) Quartet–quartet coupling.

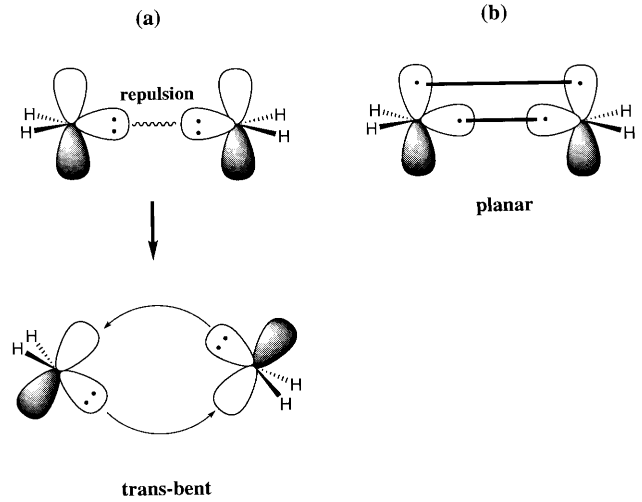

Fig. 4. Two interaction modes between MH_2. (a) Singlet–singlet coupling. (b) Triplet–triplet coupling.

of the strong interaction, the 2s level goes up and becomes close to the level of the vacant $2p_z$ orbital remaining on C. For this reason, CH has a low-lying quartet state. Because two C–H bonds are formed in CH_2, the interaction is approximately twice as large as that in CH, the 2s level becoming much closer to the $2p_z$ level. Therefore, one of two electrons in the 2s orbital occupies the $2p_z$ orbital to give the triplet ground state of CH_2. In addition, a strong interaction between the C–H bonds leads to a widening of the bond angle.

It is informative to view $HM{\equiv}MH$ as consisting of two MH units [19,20]. Two interaction modes (**a** and **b**) between MH units are shown in Fig. 3. The quartet state ($^4\Sigma$) of CH is only 16.7 kcal mol^{-1} less stable than the ground doublet state ($^2\Pi$) [21]. Therefore, mode **b** plays an important role and leads to the linear structure of $HC{\equiv}CH$. Since the doublet–quartet separation is considerably larger for the heavier MH case, mode **a** becomes dominant for $HM{\equiv}MH$. As a result, the linear structure undergoes exchange repulsion between the lone pairs on M. The M–M distance is not only elongated to avoid the repulsion but its structure is *trans*-bent [22] to gain stabilization due to electron transfer (denoted by arrows in Fig. 3). The resultant M–M bonding may be better regarded as consisting of two dative bonds and one π bond. It is interesting that the *trans*-bending of $H_2M{=}MH_2$ is also explained in the same way [19,23,24], as shown in Fig. 4; it results from the dominance of the singlet–singlet coupling of two MH_2 units, because the ground state of MH_2 is singlet, unlike the CH_2 case.

One may notice that linear $HM{\equiv}MH$ and planar $H_2M{=}MH_2$ structures have considerably short M–M bond distances upon optimization. However, it should be emphasized that bond distances are not necessarily correlated to bond strengths; the short M–M bonds are weaker than those of the *trans*-bent structures. To maintain linear and planar structures, the MH and MH_2 units must be excited from their ground states to quartet and triplet states, respectively; that is, $n\mathrm{s} \rightarrow n\mathrm{p}$ promotion is required for each M atom. To compensate for this energy loss, the M–M bond distances shorten to increase the orbital overlapping between M atoms as much as possible. However, the cost of excitation is too large to be offset just by bond shortening, leading to weaker bonds and destabilization of the linear and planar structures. This is because heavier M atoms are incapable of forming effective hybrid orbitals owing to the size difference between ns and np orbitals. It is a general trend that short yet weak bonds are often observed for molecular structures in which promotion (and concomitant hybridization) is enforced for heavier atoms [16].

We turn to the 1,2-H shifted structures, $M{=}MH_2$ and $HM{-}MH_3$. In these structures, no promotion from the $(n\mathrm{s})^2$ pair is required for the left M atom. Since the left M atom can participate in M–M bonding without hybridization, $M{=}MH_2$ and $HM{-}MH_3$ lie lower in energy than $HM{\equiv}MH$ and $H_2M{=}MH_2$, respectively. In this regard, it is instructive to consider the dibridged structure of M_2H_2 as a union of two hydrogen atoms and M=M (two M atoms connected with the $(\sigma_g)^2(\pi_u)^1(\pi_u)^1$ occupancy in the ground triplet $^3\Sigma_g^-$ state by keeping intact the $(n\mathrm{s})^2$ pairs) [25]. Since each hydrogen forms a three-center two-electron bond with one of the π orbitals at right angles to one another, no significant hybridization is enforced for both of the M atoms. This makes the dibridged structure more stable than $M{=}MH_2$.

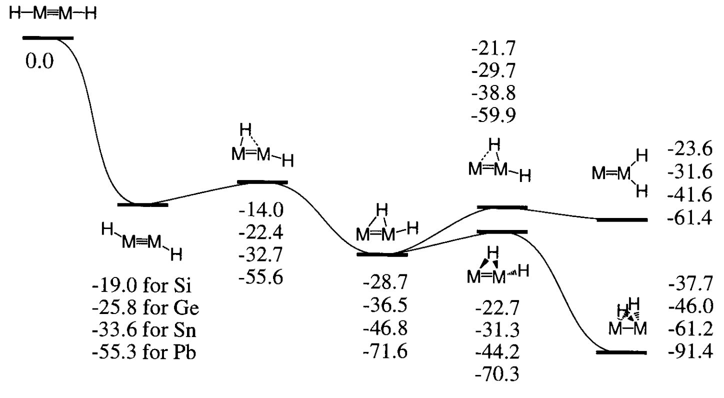

Fig. 5. The potential energy surface of M_2H_2 (M = Si, Ge, Sn, and Pb) in kcal mol^{-1}.

2.3. The potential energy surface of M_2H_2

The potential energy surfaces calculated at the MP2/6-311G(2d,2p) level with zero-point energy correction for M_2H_2 (M = Si, Ge, Sn, and Pb) are summarized in Fig. 5 [26]. As M becomes heavier, the energy difference between the linear and *trans*-bent structures of HM≡MH is highly enhanced with an increase in *trans*-bending. This is consistent with the fact that the doublet–quartet energy difference of MH increases by ca. 15 kcal mol^{-1} upon going from SiH to PbH. In addition, the barrier for isomerization of the *trans*-bent structure becomes smaller, as M becomes heavier, and dibridged structures are highly stabilized. In this context, it is notable that the mono- and dibridged structures of Si_2H_2 have been detected and characterized by using spectroscopic methods [27]. However, these bridged structures tend to be destabilized for steric reasons upon substitution and disappear from the potential energy surface of M_2R_2 as R becomes bulkier [26]. Therefore, it is important to prevent the 1,2-R shift in RM≡MR in order to maintain a disilyne structure.

2.4. Electronic and steric effects of substituents

It is an interesting subject whether the heavier analogues of alkynes are successfully synthesized and isolated as stable compounds when they are properly substituted. Thus, the effect of substituents on silicon–silicon triple bonds has been systematically investigated by performing density functional calculations at the B3LYP/3-21G* level [20].

The *trans*-bent structure of RSi≡SiR is ca. 20 kcal mol^{-1} more stable for R = H than the linear structure. This energy difference is little changed when R = Me, while it is highly decreased to 10 kcal mol^{-1} with R = SiH_3. Apparently, silyl substitution is more favorable than methyl [13d], as also found for the heavier analogues of aromatic and polyhedral carbon compounds [28]. The charge density analysis shows that SiH_3 acts as an electropositive group while Me is electronegative in RSi≡SiR. The advantage of electron-donating substituents over electron-accepting ones is most probably ascribed to the fact that the increased negative charges on triply bonded silicon atoms decrease the size and energy differences between valence s and p orbitals, making efficient hybridization facile [28,29].

To make this point clearer, substitution by different silyl groups, $SiMe_3$, $SiPh_3$, and $Si(SiH_3)_3$, was tested. The charge analysis shows that the $SiMe_3$ and $SiPh_3$ groups are more electropositive than SiH_3, while $Si(SiH_3)_3$ is slightly electronegative. Accordingly, $Si(SiH_3)_3$ tends to increase the energy difference between the linear and *trans*-bent structures of RSi≡SiR, compared with the SiH_3 case. In contrast, more electropositive $SiPh_3$ and $SiMe_3$ groups make the energy difference as small as 7.2 and 7.0 kcal mol^{-1}, respectively. It is interesting that these energy differences are related to the doublet–quartet energy differences of SiR, as shown in Table 1; the doublet–quartet closeness makes interaction mode **b** in Fig. 3 favorable and leads to the linearity of RSi≡SiR.

However, it was found that silyl groups tend to raise the HOMO level of disilynes, leading to a higher reactivity. To suppress this reactivity, bulky silyl groups, $Si(t\text{-}Bu)_3$ and $SiDep_3$ (Dep = 2,6-diethylphenyl), were considered for RSi≡SiR. The doublet–quartet energy difference of the SiR part is 18.6 kcal mol^{-1} for

Table 1
Energy differences between the doublet and quartet states of SiR and between the linear and *trans*-bent structures of RSi≡SiR in kcal mol^{-1} at the B3LYP/3-21G* level

	SiR doublet–quartet	RSi≡SiR linear-*trans*
R=H	42.6	20.3
R=Me	46.2	18.4
R=$Si(SiH_3)_3$	26.7	10.4
R=SiH_3	26.0	10.1
R=$SiPh_3$	23.5	7.2
R=$SiMe_3$	18.4	7.0

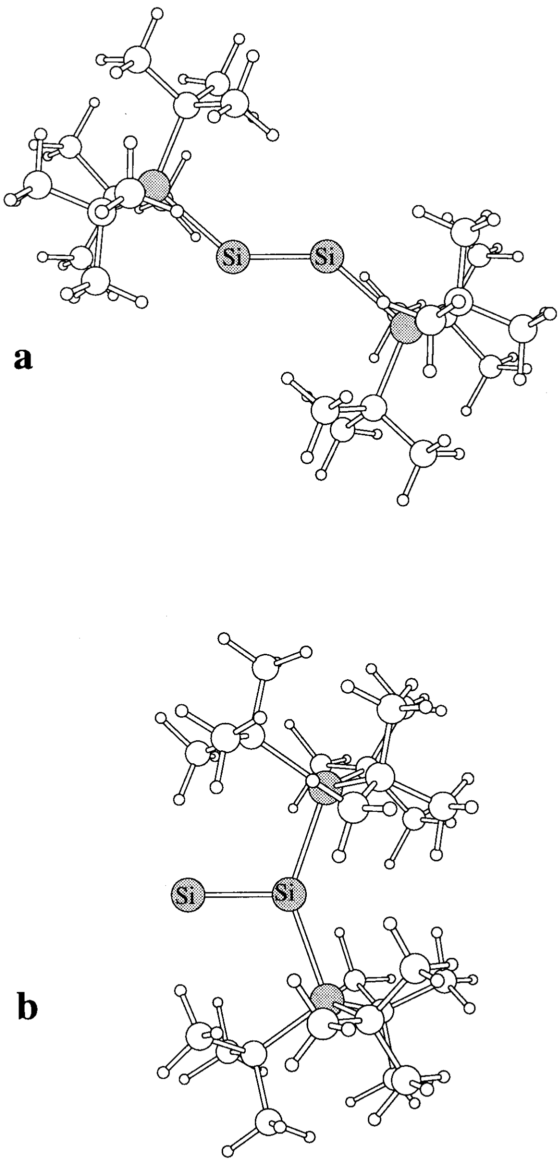

Fig. 6. Optimized structures of (a) $(t\text{-Bu})_3\text{SiSi}\equiv\text{SiSi}(t\text{-Bu})_3$ and (b) the 1,2 shifted isomer.

$R = Si(t\text{-Bu})_3$ and 29.2 kcal mol^{-1} for $R = SiDep_3$. These energy differences are comparable to and larger than that of 18.4 kcal mol^{-1} for $R = SiMe_3$, respectively. Nevertheless, the energy difference favoring the *trans*-bent structure [30] over the linear one is only 4.0 kcal mol^{-1} with $R = Si(t\text{-Bu})_3$ and 5.5 kcal mol^{-1} with $R = SiDep_3$ owing to the bulk of substituents; the *trans*-bending is 13.3 and 16.1° smaller for $R = Si(t\text{-Bu})_3$ and $SiDep_3$ than that of HSi≡SiH, respectively. In addition, these substituent groups help to protect the central silicon–silicon bond from the attack of reactive species; as clearly shown in Figs. 6 and 7, this protection is much more effectively accomplished by the bulkier $SiDep_3$ groups.

The central Si–Si bond distance is 2.068 Å for $(t\text{-Bu})_3\text{SiSi}\equiv\text{SiSi}(t\text{-Bu})_3$ and 2.072 Å for $\text{Dep}_3\text{SiSi}\equiv\text{SiSiDep}_3$. These bond distances are 0.13–0.18 Å shorter than the Si–Si double bond distances of 2.202–2.251 Å observed for silyl-substituted disilenes [31], supporting that the two silicon atoms are triply bonded. The energy required for breaking the Si–Si triple bond is 80 kcal mol^{-1} for $(t\text{-Bu})_3\text{SiSi}\equiv\text{SiSi}(t\text{-Bu})_3$. This energy is decreased for $\text{Dep}_3\text{SiSi}\equiv\text{SiSiDep}_3$ by a larger steric repulsion between the bulkier $SiDep_3$ groups, but is still as large as 56 kcal mol^{-1}. These large binding energies suggest that the silyl-substituted disilynes do not dissociate in solution, unlike the heavier (Sn, Pb, and some Ge) analogues of alkenes [1]. In addition, bulky groups can destabilize the 1,2-sifted isomers because they crowd around one end of the Si–Si bond, as shown in Figs. 6 and 7, and prevent the isomerization of disilynes. Thus, $(t\text{-Bu})_3\text{SiSi}\equiv\text{SiSi}(t\text{-Bu})_3$ and $\text{Dep}_3\text{SiSi}\equiv\text{SiSiDep}_3$ are now 9.7 and 12.0 kcal mol^{-1} more stable than the 1,2-shifted isomers, respectively.

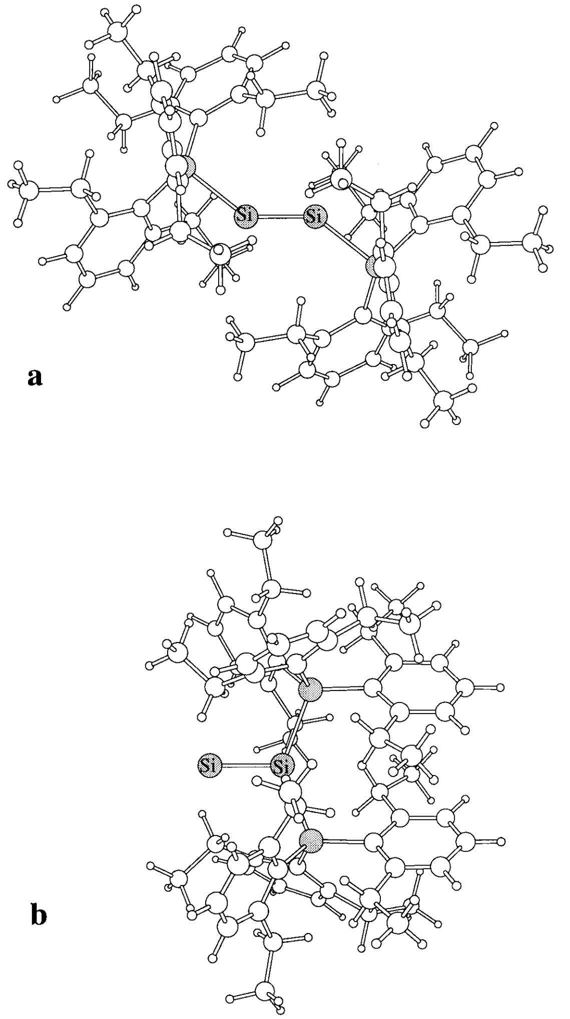

Fig. 7. Optimized structures of (a) $\text{Dep}_3\text{SiSi}\equiv\text{SiSiDep}_3$ and (b) the 1,2 shifted isomer.

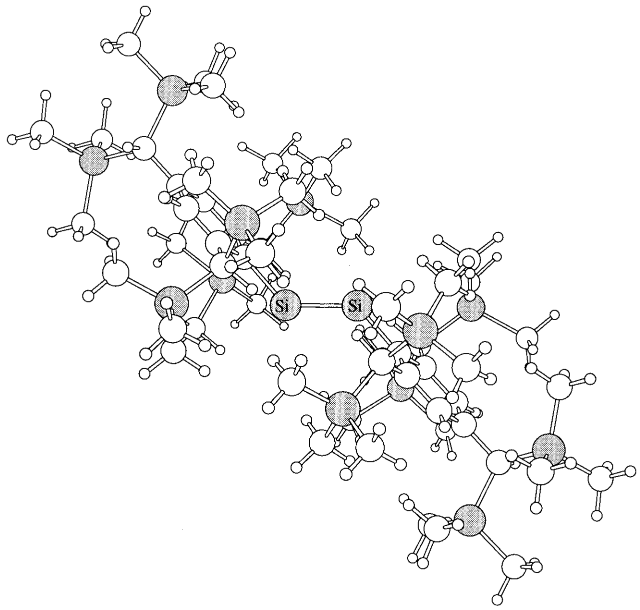

Fig. 8. Optimized structure of TbtSi≡SiTbt.

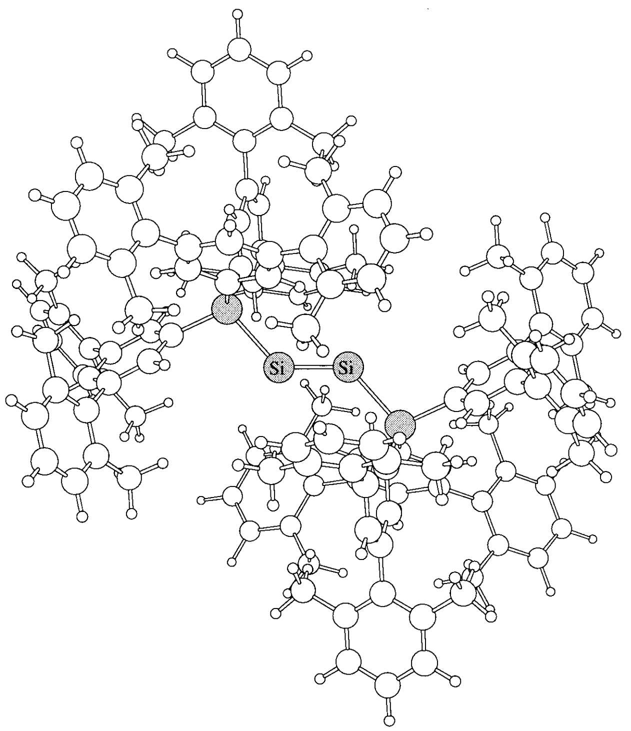

Fig. 9. Optimized structure of a disilyne protected by bulky silyl substituent groups.

The difficulty in preparing RSi≡SiR is also ascribed to the facile dimerization leading to tetrasilatetrahedranes or tetrasilacyclobutadienes ($\mathrm{Si_4R_4}$). Accordingly, it has recently been verified from preliminary experiments that tetrasilatetrahedranes are readily obtained when R is as bulky as $\mathrm{Si(}t\mathrm{\text{-}Bu)_3}$ [32]. This reflects that the dimerization of $(t\text{-Bu})_3\mathrm{SiSi{\equiv}SiSi}(t\text{-Bu})_3$ is 80 kcal mol^{-1} exothermic [33]. It is interesting that the first synthesis of tetrasilatetrahedrane was successful with $\mathrm{Si}(t\text{-Bu})_3$ groups [34]. These suggest that it is very important to utilize bulkier silyl groups in preparing disilynes.

To test the effect of bulky aryl groups, TbtSi≡SiTbt (Tbt = 2,4,6-tris[bis(trimethylsilyl)methy]phenyl [35]) was investigated at the B3LYP/3-21G* level [36]. This disilyne is interesting since it has structural resemblance to TbtSb=SbTbt and TbtBi=BiTbt synthesized and isolated recently as stable doubly bonded compounds [37]. The optimized structure of TbtSi≡SiTbt is shown in Fig. 8. Because of the electron accepting character and bulkiness of the Tbt group, the *trans*-bending is 10° larger and the Si–Si bond distance of 2.121 Å is 0.05 Å longer than those of $\mathrm{SiDep_3Si{\equiv}SiSiDep_3}$. However, TbtSi≡SiTbt is 23 kcal mol^{-1} more stable than the 1,2-Tbt shifted isomer owing to the bulkiness of Tbt, and its dissociation into two SiTbt units is 52 kcal mol^{-1} endothermic. In addition, it is noteworthy that the dimerization of TbtSi≡SiTbt is 58 kcal mol^{-1} endothermic.

Very recently, an interesting silyl group ($\mathrm{SiAr_3}$, Ar = 3,5-bis(2,6-dimethyphenyl)phenyl) was developed [38]. Substitution by this silyl group was also tested at the B3LYP/3-21G* level, as shown in Fig. 9. The Si–Si triple bond distance of 2.080 Å is 0.04 Å shorter than that in TbtSi≡SiTbt. An interesting finding is that the disilyne bearing bulky silyl groups is highly stable to both isomerization and dimerization.

3. Concluding remarks

Stable silicon–silicon triply bonded compounds are synthetically accessible when they are properly substituted (even with substituents available at present). This predication awaits experimental testing and verification. It is expected that the heavier silicon analogues of alkynes will be soon synthesized as stable compounds and open a new area of main group chemistry. A study of substituent effects on the still heavier triple bonds is in progress [39].

Acknowledgements

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