

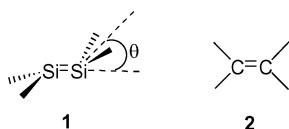
How to Design Linear Allenic-Type Trisilaallenes and Trigermaallenes

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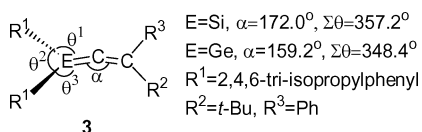
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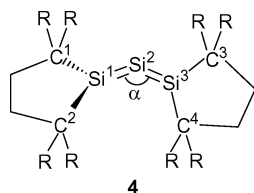
The chemistry of compounds containing multiple bonds to silicon has developed rapidly since the isolation of the first stable silene and disilene in 1981.^{1,2} A variety of compounds with C=E and E=E (E = Si, Ge, Sn, Pb) bonds were isolated, characterized,^{1,2} and studied theoretically.³ Experimental^{1,2,4} and theoretical³ studies revealed that the double-bonded compounds of silicon and its heavier group-14 analogues usually adopt trans-bent structures, **1**, in contrast to the planar carbon analogues, **2**.



In contrast to the substantial information which is already available for compounds with C=E and E=E bonds, very little is known, either experimentally⁵ or theoretically,^{3a,b} about compounds with an extended skeleton of multiple bonds of the types E=C=C, E=E=C, E=C=E, or E=E=E. The first two compounds of this type, R¹₂E=C=CR²R³ (E = Si, Ge) (**3**), were synthesized and characterized by X-ray crystallography only recently, showing a nonlinear E=C=C skeleton with a pyramidalized R¹₂E entity.⁶ A theoretical study⁷ concluded that the bending of the E=C=C skeleton is an inherent property of the molecule.



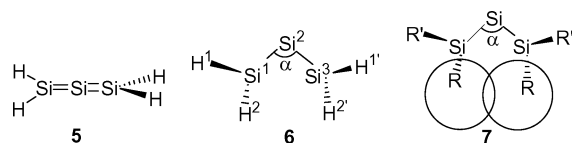
The first group 14 compound containing an E=E=E allene-type skeleton, (*t*-Bu₃Si)₂Sn=Sn=Sn(Si*t*-Bu₃)₂, was reported in 1999, showing a bending angle of 155.9° at the central tin atom and significant pyramidalization at the terminal tin atoms.⁸ In 2003, Kira et al. reported the spectacular isolation of the first trisilaallene **4** (R = Me₃Si) which exhibits a very acute Si=Si=Si angle of 136.5°, and quantum mechanical calculations showed that R₂Si=Si=SiR₂ (R = CH₃) also possesses a **bent** Si=Si=Si skeleton.⁹



The strongly bent structures of **4** (R=Me₃Si) and of (*t*-Bu₃-Si)₂Sn=Sn=Sn(Si*t*-Bu₃)₂ raise the intriguing question: Can heavier group-14 analogues of allene be linear? In this contribution we provide, using high-level, up-to-date quantum mechanical calculations,

a theoretical prescription which shows how to design a linear allenic-type, R₂E=E=ER₂ (E = Si, Ge).

Quantum mechanical calculations^{10a,11} show that the linear (*D*_{2d} symmetry) trisilaallene **5** is not a minimum on the Si₃H₄ potential energy surface (PES) but is a second-order saddle point. Upon breaking the *D*_{2d} symmetry **5** optimizes to an unusual highly bent structure **6** of *C*_s symmetry with a bending angle α of 69.4°, planar terminal silicon atoms and dihedral angles $\angle\text{H}^1\text{Si}^1\text{Si}^3\text{H}^{1'} = 0^\circ$ and $\angle\text{H}^1\text{Si}^1\text{Si}^3\text{H}^{2'} = 115.5^\circ$ (the respective angles in allene and in **5** are 90° and -90°). Upon bending of **5**, the Si=Si double bonds are elongated from 2.125 Å in **5** to 2.269 Å in **6** (B3LYP/6-31G-(d,p)).¹² Linear **5** lies 20.6 kcal/mol above **6**.¹³

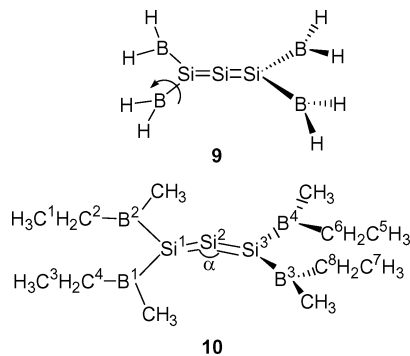


Can a proper substitution be found that will restore the linear allenic-type structure for a trisilaallene? Substitution of **5** with four methyl groups has a small effect; the SiSiSi bond angle is slightly widened to 74.2°,¹⁴ probably as a result of steric congestion between the methyl groups, as shown in **7**. Increasing the steric congestion by using bulkier alkyl groups widens α to 116.9° for R=(H₃CH₂C)₂-(H₃C)C (R'=CH₃) (it also twists the planes of the terminal R'Si groups to be almost perpendicular to each other). Similar steric effects are responsible for the relatively wide α angle of 136.5° in **4** (R=Me₃Si) (geometry optimization of **4** (R = H) results in $\alpha = 86.6^\circ$ with the skeletal C¹C²Si¹Si²Si³C³C⁴ atoms being in the same plane). It is clear that the strategy of increasing the substituents' size does not lead to the desired *D*_{2d}-allenic-type trisilaallene.

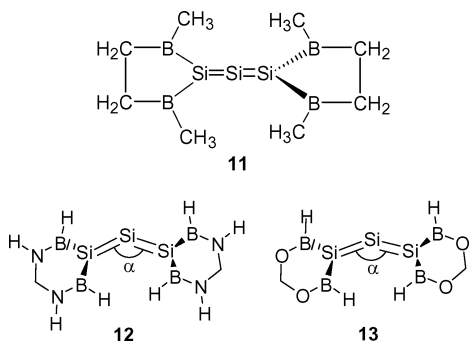
Silyl substitution has a much more profound effect on the central bending angle, and in (H₃Si)₂Si=Si=Si(SiH₃)₂ (**8**) α is 126.7°. Furthermore, in **8** the planes defined by the terminal (H₃Si)₂Si fragments are perpendicular to each other, as in allene, while in **7** (R = R' = CH₃) they are very similar to those of **6**. The energy required to enforce an allenic-type linear structure for **7** (R = R' = CH₃) and for **8** is 16.8 and 4.7 kcal/mol, respectively. These energy differences demonstrate that with more electropositive substituents, such as SiH₃, the bending potential of α is flatter, and thus, linearization becomes more feasible. Therefore, the way to reach a *D*_{2d} structure seems to be the use of electropositive substituents.

Indeed, substitution of trisilaallene with H₂B groups achieves the goal! In **9** the SiSiSi skeleton is linear, the terminal silicon atoms are planar, and the two terminal BSiB planes are perpendicular to each other — yielding a classic allenic-type *D*_{2d} structure! The Si=Si double bond length in **9** is 2.207 Å, somewhat elongated compared to that of **5** (2.125 Å) but shorter than that in **6** (2.269 Å). NBO analysis^{10b} (B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p)) reveals significant conjugation between the BH₂ groups and the Si=Si

bonds, so that each of the Si=Si bonds is depopulated to 1.68 eI. while the empty 2p orbital of each B is populated with 0.16 eI. Rotation of one of the BH₂ groups by 90° (with constrained C_s symmetry) requires 8.1 kcal/mol demonstrating the significant 2p(B)– π (Si=Si) conjugation.¹⁵ The crucial role of conjugation between the Si=Si bonds and the empty 2p(B) orbitals in inducing linearity of the Si=Si=Si skeleton is clearly demonstrated in **10**. That is when the hydrogens on the boron atoms in **9** are substituted by a bulky alkyl group represented by Et whose orientation was constrained so as to mimic a steric repulsion similar to that caused by a *t*-Bu group^{16a,b} and by Me, a bent structure **10**, with $\alpha = 171.0^\circ$ results.^{16c} The steric congestion between the constrained Et groups forces the BR₂ groups to rotate by 21.6°, reducing the 2p(B)– π (Si=Si) conjugation.



To prevent rotation around the Si–B bonds, cyclic diboryl substituents as in **11** can be used. **11** is indeed found to have a classic allenic-type structure with a Si=Si bond length of 2.173 Å and perpendicular siladiboryl rings. **11** is a system which potentially can be synthesized. It is interesting that in contrast to **11**, **12** and **13** have strongly bent structures with α of 137.5° and 145.8°, respectively. This is primarily due to reduced 2p(B)– π (Si=Si) conjugation as a result of competing 2p(N)–2p(B) or 2p(O)–2p(B) conjugation.



The optimized structure of H₂Ge=Ge=GeH₂ is bent, with $\alpha = 70.9^\circ$ and $r(\text{Ge}=\text{Ge})$ of 2.367 Å. However, (H₂B)₂Ge=Ge=Ge–(BH₂)₂ and the Ge analogue of **11** have an allenic-type linear structure and a shorter Ge=Ge bond of 2.268 Å and 2.231 Å, respectively.

In summary, linear trisilaallenes and trigermaallenes do exist when σ -donor, π -acceptor R₂B substituents are used. Very bulky silyl substituents may also induce a linear allenic-type structure due to the small linearization barriers in these trisilaallenes. These theoretical predictions, and in particular the prediction that **11** has an allenic-type structure, are awaiting experimental testing.

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Supporting Information Available: Cartesian coordinates and total energies. This material is available free of charge via Internet at <http://pubs.acs.org>

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- (12) Similar structures were calculated also using ab initio methods which include electron correlation such as MP2/6-31G(d,p) and CCD/6-311++G-(2df,p).
- (13) Structure **6** is the global minimum on the H₄Si₃ PES; the trisilacyclopropylidene isomer is by 3 kcal/mol higher in energy. A detailed study of the Si₃H₄ PES will be published elsewhere.
- (14) A second minimum with $\alpha = 92.5^\circ$ (identical to that reported in ref 9) was also located. It is by only 0.1 kcal/mol higher in energy, which indicates that the bending potential of **7** is very flat.
- (15) We note that the boryl substituents also stabilize thermodynamically the trisilaallene. According to the isodesmic reaction: $\mathbf{9} + 2\text{Me}_2\text{SiH}_2 \rightarrow 2(\text{BH}_2)_2\text{SiH}_2 + \mathbf{7}$ (R = R' = CH₃), **9** is thermodynamically more stable than **7** (R = R' = CH₃) by 30.9 kcal/mol.
- (16) (a) The dihedral angles C¹C²B²Si¹, C³C⁴B¹Si¹, C⁵C⁶B⁴Si³, and C⁷C⁸B³Si³ were constrained to 0.0°, 60.0°, 60.0°, and 0.0°, respectively. (b) The fully optimized structure of **10** has a D₂-allenic-type structure, with a linear Si=Si=Si skeleton, and the B¹Si¹B² and B⁴Si³B³ planes are perpendicular to each other. (c) The Si¹ and Si³ centers are not planar, i.e., $\angle\text{B}^1\text{Si}^1\text{B}^2\text{Si}^2$ and $\angle\text{B}^3\text{Si}^3\text{B}^4\text{Si}^2$ are -163.1° and 166.3° , respectively.

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