Reaction of cyclotrisilene with phenylacetylene: an unusual product with a bicyclo[3.2.0]hepta-3,6-diene skeleton†

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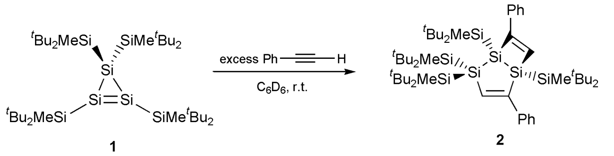
Cyclotrisilene, (^{t}Bu$_2$MeSi)$_4$Si$_3$, was reacted with phenylacetylene to produce an unusual 1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene derivative, whose structure was determined by NMR spectroscopy and X-ray crystallography; a mechanism for its formation is proposed.

The synthesis and characterization of a number of isolable double bond species consisting of the heavier Group 14 elements has been accomplished since the first isolation of tetramesityldisilene by West *et al.* in 1981.[1,2] Cyclotrimetallenes (R_4M_3, M = Si, Ge, Sn), *i.e.* compounds with endocyclic metal–metal double bonds, have been prepared: cyclotrigermenes in 1995,[3] cyclotrisilenes in 1999,[4,5] and cyclotristannene in 1999.[6] Quite recently, we have succeeded in the preparation of the first mixed cyclotrimetallenes consisting of two different Group 14 elements: 1- and 2-disilagermirenes.[7] These compounds exhibit an enhanced reactivity arising from the combination of a highly reactive metal–metal double bond and a highly strained three-membered ring skeleton in one molecule, which gives access to new cyclic and bicyclic compounds by addition and cycloaddition reactions.[8] Recently, we have also succeeded in transforming the cyclotrigermenes and cyclotrisilene into the cyclotrigermenylium ions[9] and cyclotetrasilenylium ion,[10] which are free germyl and silyl cations, respectively. Herein, we report on the reaction of cyclotrisilene **1** with phenylacetylene to produce an unusual product with a bicyclo[3.2.0]hepta-3,6-diene skeleton, and report also on its reaction mechanism.

Cyclotrisilene **1** was allowed to react with excess phenylacetylene in C_6D_6 at rt. The orange colour of **1** disappeared within 15 h to give a 1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene derivative **2** in a 65% yield (Scheme 1). No reaction occurred with trimethylsilylacetylene, bis(trimethylsilyl)acetylene, or diphenylacetylene, and a complicated reaction mixture was formed with hex-1-yne.

The structure of **2** was determined by mass spectrometry, NMR spectra and X-ray crystallography. The mass spectrum of **2** showed a very weak parent ion at 916, with fragmentation peaks at 859 ($M^+ - {}^t$Bu) and at 759 ($M^+ -$ SiMe^{t}Bu$_2$). The ^{1}H NMR spectrum showed two olefinic protons at 7.42 and 7.98 ppm, as well as peaks indicating the presence of four different ^{t}Bu$_2$MeSi groups, and two phenyl groups. The ^{13}C and ^{29}Si NMR spectra were also consistent with this structure being a 1:2 adduct of **1** and phenylacetylene. As shown in Fig. 1, compound **2** has a bicyclo[3.2.0]hepta-3,6-diene skeleton, the formation of which can be explained by the consecutive addition of one molecule of phenylacetylene to the Si=Si double bond, and by the insertion of a second molecule of phenylacetylene into the Si–Si single bond in the resulting cyclotrisilane ring. The cycloaddition reaction of acetylenes with a Si=Si double bond to give the disilacyclobutene derivative is well known,[11] but the insertion of C–C multiple bonds into a Si–Si single bond at ambient temperature without the use of a catalyst has not been reported.



Scheme 1

The formation of **2** was quite interesting for us, and prompted us to investigate its formation mechanism. Under the same conditions as above, deuterium-labelled cyclotrisilene, **1–d$_6$**,[12] in which the CH_3 groups in the di-*tert*-butyl(methyl)silyl substituents on the saturated silicon atom were replaced by a CD_3 group, was reacted with phenylacetylene to give **2a–d$_6$** and **2b–d$_6$** in a 1:1 molar ratio.[13] This result indicates that **2** is not formed *via* a simple [2 + 2] cycloaddition and insertion process. A more likely mechanism is as follows. First, the phenylacetylene undergoes cycloaddition to the Si=Si double bond of **1–d$_6$** to form the 1,4,5-trisilabicyclo[2.1.0]pent-2-ene derivative **3–d$_6$**, which then isomerizes to the 1,2,3-trisilacyclopenta-3,5-diene derivative **4–d$_6$**, which has a conjugated Si=C–C=Si system in a five-membered ring. Secondly, one ^{t}Bu$_2$(CD$_3$)Si group on a saturated silicon atom migrates to an unsaturated silicon atom to give the 1,2,3-trisilacyclopenta-2,4-diene derivative **5–d$_6$**, which has a conjugated Si=Si–C=C system in a five-membered ring.[14] Finally, the silole intermediate **5–d$_6$**, is trapped by phenylacetylene *via* a [2 + 2] cycloaddition across

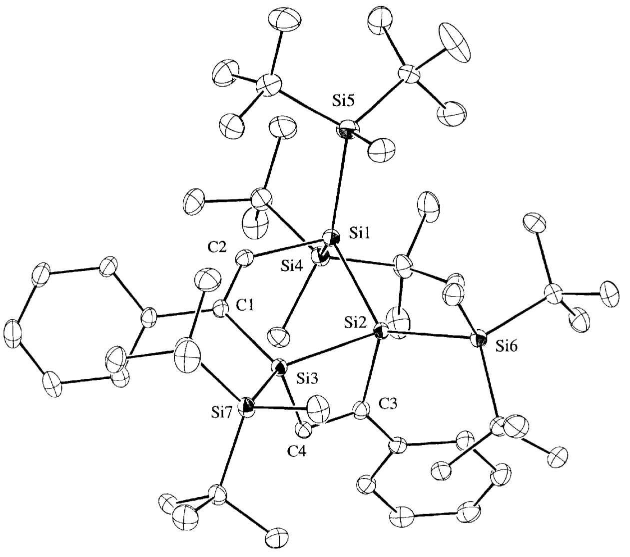


Fig. 1 Structure of **2** (hydrogen atoms are omitted for clarity). Selected bond distances [Å] are: Si1–Si2 2.477(1), Si1–C2 1.893(3), Si2–Si3 2.388(1), Si2–C3 1.943(3), Si3–C 11.909(3), Si3–C4 1.892(3), C1–C2 1.351(4), C3–C4 1.356(4). Selected bond angles [°] are: Si2–Si1–C2 95.8(1), Si1–Si2–Si3 92.6(0), Si3–Si2–C3 73.7(1), Si2–Si3–C1 101.7(1), Si2–Si3–C4 75.0(1), Si3–C1–C2, 119.0(2), Si1–C2–C1 130.5(2), Si2–C3–C4 104.7(2), Si3–C4–C3 106.5(2).

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† Electronic supplementary information (ESI) available: experimental procedure, spectral data and X-ray data (CCDC 182/1876) of the products. See http://www.rsc.org/suppdata/cc/b0/b008375p/

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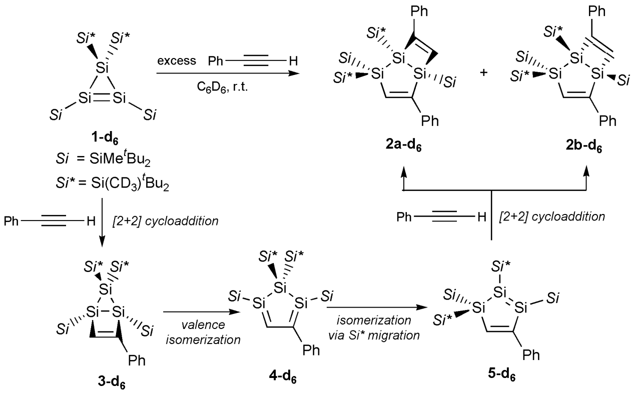
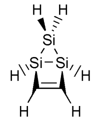


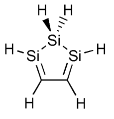
Scheme 2

the Si=Si double bond to afford a mixture of **2a**–$\mathbf{d}_6$ and **2b**–$\mathbf{d}_6$ (Scheme 2). However, the silole intermediates **4** and **5** were not observed in monitoring the reaction of **1** with phenylacetylene using NMR spectroscopy, which is probably due to their high reactivity. Even with equimolar quantity of phenylacetylene, the product **2** was formed together with unreacted **1**.

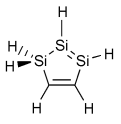
To have a better understanding of the isomerization of **3** to **5**, *ab initio* calculations on the parent system (**6**–**8**) were carried out at the Beck3LYP/6-31G(d) level, and all isomers **6**–**8** were found as energy minimum structures. The bicyclic structure **6** was the most unfavourable, probably due to the highly strained three- and four-membered bicyclic structure, and the siloles **7** and **8** were more stable by 1.0 and 13.1 kcal mol^{-1} relative to **6**, respectively. The conrotatory isomerization of **6** to **7** may be unfavourable because of the fixed bicyclic structure of **6**. The last compound consequently isomerizes by the migration of the hydrogen atom to give the thermodynamically most stable silole structure **8**, with a Si=Si–C=C conjugated system.



6 (0.0 kcal mol^{-1})



7 (-1.0 kcal mol^{-1})



8 (-13.1 kcal mol^{-1})

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12 Cyclotrisilene **1**–$\mathbf{d}_6$ was prepared by the reductive condensation of 2,2-dibromo-1,1,3,3-tetra(*tert*-butyl)-1,3-bis-(trideuteriomethyl)trisilane and 2,2,2-tribromo-1,1-di-(*tert*-butyl)-1-methyldisilane with sodium in toluene. See ref. 5.

13 The signal at 0.67 ppm assigned to a methyl group on Si6 completely disappeared, and the relative intensities of two signals at 0.16 and 0.51 ppm, assigned to the methyl groups on Si4 and Si5, were half the magnitude of those of **2**.

14 Thermal rearrangement of tetrakis[di-*tert*-butyl(methyl)silyl]-1-disilagermirene to tetrakis[di-*tert*-butyl(methyl)silyl]-2-disilagermirene by $^t\text{Bu}_2\text{MeSi}$ group migration was reported. See ref. 7.