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Communications

Addition of a Cyclopropyl Alkyne to Tetramesityldisilene: Evidence for a Biradical Intermediate and Formation of a Stable 1,2-Disilacyclohepta-3,4-diene

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Summary: The intermediate formed during the addition of an alkyne to tetramesityldisilene has been determined to be a biradical by the use of a newly developed mechanistic probe, designed to discriminate among vinyl radicals, cations, and anions.

The addition of alkynes to disilenes to give 1,2-disilacyclobutenes is a well-known reaction of disilenes.[1] It was one of the first addition reactions examined after the synthesis of the first stable derivatives of disilenes[2] and alkynes continue to serve as important trapping reagents, particularly in systems where both the disilene and the silylene may be present.[3] However, despite the critical role of this reaction in disilene chemistry, little is known about the mechanism by which it proceeds. Only two studies have been reported which provide some insight into the mechanism of the addition. Sakurai found that when *trans*-1,2-dimethyl-1,2-diphenyldisilene was generated by thermolysis of the appropriate disilabicyclooctadiene in the presence of diphenylacetylene, a mixture of diastereomeric 2,5-dimethyl-2,3,4,5-tetraphenyl-1-oxa-2,5-disilacyclopentenes (from the stereoselective oxidation of the disilacyclobutenes) was formed after exposure of the reaction mixture to the ambient atmosphere.[1m] A similar result was obtained when diphenylacetylene was added to *cis*-1,2-dimethyl-1,2-diphenyldisilene. The stereochemical scrambling implies the formation of an intermediate that allows for rotation about the Si−Si bond. The authors suggested the formation of a biradical intermediate, although no experimental evidence for one was provided. West *et al.*[1j,k] reported that when tetramesityldisilene was allowed to react with a variety of alkynes, disilacyclobutene adducts were only obtained

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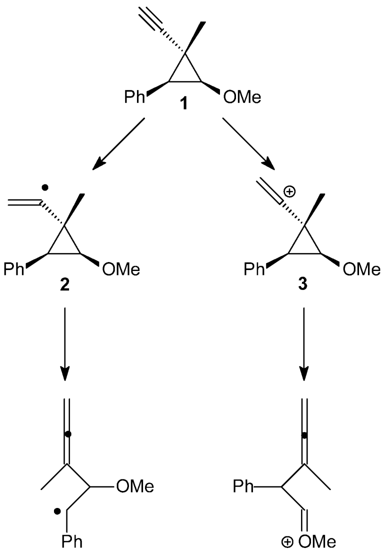
Scheme 1. Reactivity of Vinylic Intermediates Derived from Cyclopropyl Alkyne 1

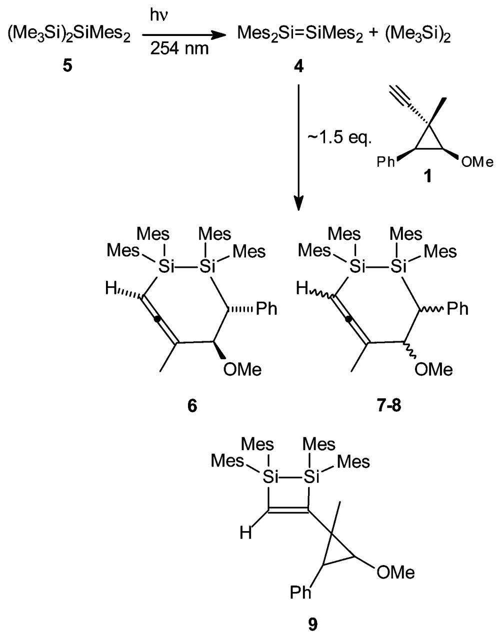


with polar alkynes such as carbomethoxy-, phenyl-, trimethylsilyl-, and ethoxyacetylene. Less polar alkynes such as 1-hexyne, diphenylacetylene, propyne, acetylene, phenyl(trimethylsilyl)acetylene, and dimethyl acetylenedicarboxylate did not react with the disilene, even after several hours of heating. The cycloaddition products were isolated as air-stable solids. When *trans*-1,2-di-*tert*-butyl-1,2-dimesityldisilene was allowed to react with alkynes, scrambling of the stereochemistry about the silicon atoms in the disilacyclobutene products was observed,[1j,k] similar to Sakurai's results. These observations led West to postulate that an intermediate was formed and, since only polar alkynes were observed to react with the disilenes, the intermediate might be zwitterionic in nature. These two studies have clearly established the formation of an intermediate during the addition of alkynes to disilenes; however, the type of intermediate is unclear.

We have recently developed a new mechanistic probe for the discrimination between vinyl radical and ionic intermediates based on cyclopropyl-substituted alkynes such as **1** (Scheme 1).[4] We have shown that the vinyl radical **2** undergoes a fast and regioselective rearrangement toward the phenyl substituent, whereas the corresponding vinyl cation, **3**, undergoes a fast and regioselective rearrangement toward the methoxy substituent. In contrast, an analogous vinyl anion (without the methyl and methoxy substituents), as modeled by the lithium derivative, did not show any evidence for ring-opening rearrangement. Herein, we report on the addition of alkyne **1** to tetramesityldisilene (**4**). We believe that the structure of the addition products will provide unambiguous information regarding the nature of the intermediates formed during the addition of alkynes to disilenes.

Alkyne **1** was added to the deep yellow solution of **4**, generated by photolysis of bis(trimethylsilyl)dimesitylsilane (**5**). The mixture was stirred for 18 h at room temperature. Analysis of the crude product by ^{1}H NMR spectroscopy revealed a mixture of **6**−**9** (44:21:14:21, respectively; Scheme 2) and the starting alkyne; very few signals remain unassigned. Although **6** and **9** could be isolated from the mixture, compounds **7** and **8** could not be separated from one another.

Scheme 2. Addition of Alkyne 1 to Disilene 4



The presence of two different ^{29}Si signals in the ^{1}H−^{29}Si gHMBC spectrum of disilacyclobutene **9** as well as signals corresponding to four different mesityl groups in the ^{1}H NMR spectrum of **9** are consistent with a lack of symmetry in the molecule. Signals at 173.98 and 155.25 ppm were observed in the ^{13}C NMR spectrum of **9** and were assigned to the vinyl ring carbon atoms of a dimetallacyclobutene ring. The chemical shifts are comparable to the chemical shifts of the analogous carbons in other dimetallacyclobutenes.[1a,b,5] The relative stereochemistry of the phenyl, methoxy, and methyl substituents on the cyclopropyl ring was difficult to assign unambiguously using the coupling constant of the vicinal ring ^{1}H's (4.7 Hz).[6]

The structure of **6** was determined by NMR and IR spectroscopy and mass spectrometry[7] and unambiguously confirmed by X-ray crystallography.[8] Both enantiomers were present in the unit cell. The molecular structure of one enantiomer of **6** is presented in Figure 1. The Si−Si bond length of 2.5428(18) Å is significantly longer than an average Si−Si bond (2.35 Å). This is likely due to the high steric congestion of the bulky mesityl groups and the high degree of ring strain

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[6] Typical coupling constants for the 2,3-*cis* ^{1}H's in *trans,trans*-2-alkoxy-3-phenyl-substituted cyclopropyl rings range from 6 to 8 Hz. (see ref 4 and: Samuel, M. S.; Baines, K. M. *J. Am. Chem. Soc.* **2003**, *125*, 12702). The coupling constants for the analogous ^{1}H's in *trans* isomers are generally 2−4 Hz (see: Sugawara, M.; Yoshida, J. *Synlett* **1998**, 1057. Wenkert, E.; Alonson, M. E.; Buckwalter, B. L.; Sanchez, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 2021. Sato, K.; Hagiwara, H.; Uda, H.; Sato, M.; Harada, N. *J. Am. Chem. Soc.* **1976**, *98*, 8281).

[7] A complete discussion of the determination of the structure of **6** by NMR and IR spectroscopy is given in the Supporting Information.

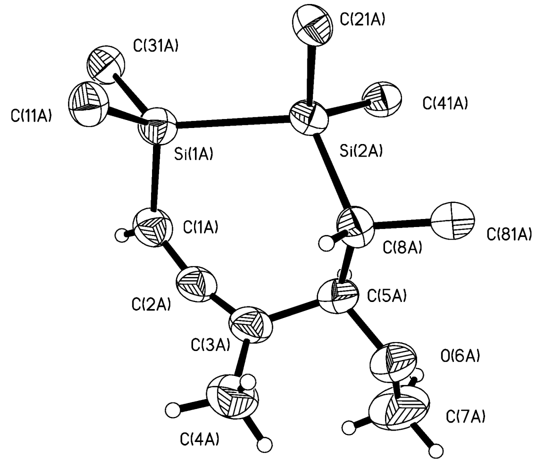

Figure 1. Core structure of **6**. Thermal ellipsoids are drawn at the 50% probability level. Only ipso carbons of the mesityl and phenyl substituents are shown for clarity. Selected bond lengths (Å) and angles (deg): Si(1A)−Si(2A) = 2.5428(18), Si(1A)−C(1A) = 1.879(5), C(1A)−C(2A) = 1.307(6), C(2A)−C(3A) = 1.293(6), Si(2A)−C(8A) = 1.997(5); C(1A)−Si(1A)−Si(2A) = 102.12(16), C(8A)−Si(2A)−Si(1A) = 112.18(14), C(3A)−C(2A)−C(1A) = 162.5(5).

present in **6**. The strain is also evidenced by the distorted C═C═C bond angle (162.5(5)°) as well as distortion about the silicon atom (C(1A)−Si(1A)−C(11A), 117.01(18)°; C(1A)−Si(1A)−C(31A), 101.31(18)°; C(31A)−Si(1A)−Si(2A), 127.04(11)°) and about the allene moiety (Si(1A)−C(1A)−[C(2A)]−C(3A)−C(4A), 101.1°; Si(1A)−C(1A)−[C(2A)]−C(3A)−C(5A), −60.0°). The metrics for the second independent molecule are comparable.

The formation of the strained cyclohepta-1,2-diene is, in itself, interesting. Chemists have long been fascinated by strained organic compounds, including cyclic allenes.[9] The unstrained allenic moiety adopts a linear arrangement of the three unsaturated carbons and an orthogonal relationship for the substituents at each end of the allene. Incorporation of the allenic group into a small ring imparts significant strain on the molecule. To alleviate the strain, bending at the central carbon and twisting of the substituent planes is commonly observed. In general, cyclohepta-1,2-dienes exist as transient intermediates;[9c] however, they can be stabilized by complexation to metals.[10] A limited number of isolable seven-membered cyclic allenes have been reported to date; in each case, a 1,2,3,4-tetrasilacyclohepta-5,6-diene ring system has been reported.[11] Sila substitution is a common strategy that has been employed for the isolation of other strained ring systems such as small-ring *trans*-alkenes and alkynes.[9b,12] The longer Si−C and Si−Si bond lengths undoubtedly decrease the strain associated with small-ring allenes and permit the isolation of such compounds. The structure of compound **6** illustrates that a stable compound containing a cyclohepta-1,2-diene can be achieved with only two carbon atoms in the ring substituted by silicon. Accordingly, the bending at the allene is more severe in compound **6** compared to the 1,2,3,4-tetrasilacyclohepta-5,6-dienes (163° versus ∼174° [11a,b]) and the Si−Si bond length is elongated (Si−Si: 2.54 Å versus 2.34 Å[11a,b]). Elongation of the Si−Si bond, however, may also be a consequence of the bulky substituents.

From the spectroscopic data of **7** and **8**, it is clear that these compounds are isomers of **6**.[7] A detailed examination of the data revealed that both **7** and **8** have the same regiochemistry as **6**; that is, the phenyl group is attached to the carbon adjacent to the silicon atom in the seven-membered ring. We were unable to unequivocally determine the stereochemistry of these isomers.

The cyclopropyl ring is no longer intact in disilacycloheptadienes **6**−**8**. Cyclopropyl ring opening is consistent with the formation of a reactive intermediate during the course of the reaction. The relative position of the phenyl substituent within disilacycloheptadienes **6**−**8** has been determined to be adjacent to the silicon atom in all isomers by NMR spectroscopy and confirmed by X-ray crystallography for **6**. This regiochemistry is only consistent with rearrangement of a cyclopropylvinyl *radical* toward the phenyl group and provides unambiguous evidence that the addition of alkyne **1** to tetramesityldisilene occurs through a stepwise reaction mechanism via the formation of a biradical intermediate, as shown in Scheme 3. The 1,4-biradical intermediate can then either cyclize to form disilacyclobutene **9** or regioselectively rearrange toward the phenyl substituent to form a new 1,7-biradical, which can then close to yield the observed disilacycloheptadienes **6**−**8**.

The formation of **6**−**8** is not consistent with a mechanism in which a zwitterionic intermediate is formed: if a cation were generated adjacent to the cyclopropyl ring, the evidence indicates that the rearrangement would occur toward the methoxy substituent, and if an

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(8) Crystal data for **6**: $C_{49}H_{58}OSi_2$, $M_r = 719.13$, triclinic, space group $P\bar{1}$, $a = 15.9840(8)$ Å, $b = 16.6589(7)$ Å, $c = 17.1723(6)$ Å, $\alpha = 74.628(3)°$, $\beta = 74.146(3)°$, $\gamma = 77.839(2)°$, $V = 4193.9(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.139$ Mg/m^3, $F(000) = 1552$, $T = 295(2)$ K, λ(Mo Kα) = 0.119 mm^{-1}. The data were collected using ψ scans and ω scans with κ offsets in the range of $-19 \leq h \leq 18$, $-15 \leq k \leq 19$, $-20 \leq l \leq 20$. Of 32 293 reflections collected, 14 711 were unique ($R_{merge} = 6.4$). Final R1($I > 2\sigma(I)$) = 0.0781; wR2 = 0.2008. R indices (all data): R1 = 0.1903, wR2 = 0.2526. Maximum and minimum heights in the final Fourier difference map were 0.554 and −0.464 e Å^{-3}. Crystals of **6** were grown from a concentrated acetone solution. A colorless plate (0.13 × 0.31 × 0.80 mm) was mounted on a glass fiber. Data were collected at room temperature (22 °C) on a Nonius Kappa-CCD diffractometer with COLLECT (Nonius BV, 1997−2001). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN (Otwinowski and Minor, 1997). The data were scaled using SCALEPACK (DENZO-SMN). The SHELXTL-NT version 6.1 (G. M. Sheldrick) suite of programs was used to solve the structure by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located. CCDC-266534 (**6**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; (+44)1223-336-033; deposit@ccdc.cam.ac.uk).

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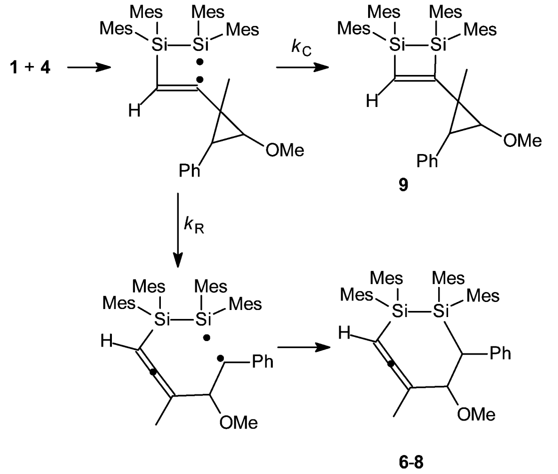
Scheme 3. Mechanism for the Formation of 6−9



anion were generated adjacent to the cyclopropyl ring, the evidence indicates that no rearrangement would occur. The formation of disilacyclobutene **9** indicates that ring closure (k_C) of the intermediate 1,4-biradical effectively competes with the ring-opening rearrangement.

While these results initially appear to contradict West's report that tetramesityldisilene (**4**) was only found to react with polar alkynes such as phenyl-, carbomethoxy-, trimethylsilyl-, and ethoxyacetylene,[1j,k] a biradical mechanism is, in fact, consistent with the experimental results. While the aforementioned alkynes are polar in nature, the substituents on the triple bond are also capable of stabilizing an α-radical.

The addition of acetylene[13] and, more recently, butadiyne[14] to the silicon dimers of a reconstructed Si(100) 2 × 1 surface has attracted much attention.[15] Although the bonding in molecular disilenes and the silicon dimers of the reconstructed Si(100) 2 × 1 surface may not be the same, it is surprising that few comparisons have been made between the reactivity of molecular disilenes and the surface disilenes. We believe that such a comparison may be instructive. Of particular relevance to this work are two theoretical studies concerning the details of the addition of acetylene and butadiyne to the Si(100) 2 × 1 surface.[14b,16] In both reports, the [2 + 2] cycloaddition was found to proceed through a biradical intermediate. Our results suggest that the reactivities of both molecular and surface disilenes may indeed be comparable.

In summary, by examination of the structure of the products obtained upon addition of the mechanistic probe **1** to tetramesityldisilene, we have provided strong evidence for the formation of a biradical intermediate. Furthermore, we were able to isolate a relatively rare example of a stable cyclohepta-1,2-diene. We continue to explore the generality of these findings.

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Supporting Information Available: Text, tables, and figures giving a discussion of the spectroscopic data of **6** (including a scheme and a table), ^{1}H NMR spectra of compounds **6**−**9**, general experimental details, experimental details for the formation of compounds **6**−**9**, and spectroscopic data for compounds **6**−**9** and a CIF file giving crystallographic information for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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