

these atoms, in contrast to other examples of η^2 -bridging CO ligands.^{1,3,14} Each ligand serves as a four-electron donor. Two electrons are donated by the carbon atom to the pair of metal atoms that it bridges, and two electrons from the oxygen are donated to the metal Ru(8). Since the oxygen atoms of both bridging carbonyl ligands are bonded to the same metal atom, the carbon atoms are brought into an unusually close nonbonding contact: C(53)···C(63) = 2.46 (2) Å. Similar close contacts have been shown to facilitate the formation of carbon-carbon bonds between CO ligands under reducing conditions.¹⁵ Efforts to achieve this are in progress.

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Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters (27 pages); tables of observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of a Tetrasilacyclohexyne¹

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Although strained cycloalkynes have received considerable experimental² and theoretical³ attention for many years, the smallest isolable rings are seven-membered.⁴ We report here the synthesis, chemical and structural characterization, and ab initio calculations of the first isolable⁵ six-membered ring containing a carbon-carbon triple bond.

In a continuation of our program of synthesis and study of silylene-acetylene polymers⁶ we were surprised to find that pentasilacycloheptyne (**2**)⁷ could be directly synthesized in 80% yield simply by the condensation of dilithioacetylene⁶ and 1,5-dichlorodecamethylpentasilane (**1**). Considerably more surprising was the discovery that the analogous coupling of LiC≡CLi and 1,4-dichlorooctamethyltetrasilane (**3**) afforded octamethyl-

Table I. NMR Comparison of Cycloalkynes **2**, **4**, and **5**

cycloalkyne	¹³ C NMR [C≡C/SiCH ₃] (δ)	²⁹ Si NMR (δ)
Me ₃ SiC≡CSiMe ₃	113.02/0.10	
c-(Me ₂ Si) ₆ C≡C, 5	117.77/-3.10, -5.14, -6.24	-35.4, -38.9, -39.9
2	123.22/-3.16, -5.91, -6.04	-33.3, -34.7, -38.7
4	135.66/-3.02, -6.51	-17.8, -30.6

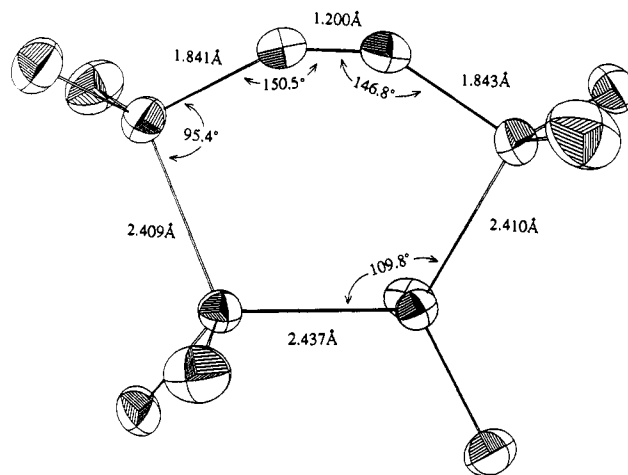
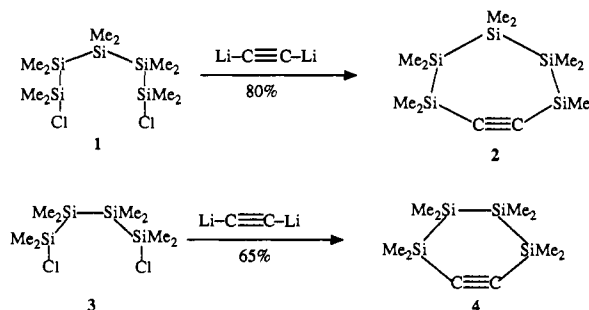


Figure 1. ORTEP diagram of octaisopropyltetrasilacyclohexyne (**8**). The methyl groups have been omitted for clarity.

tetrasilacyclohexyne (**4**) in 65% yield as a colorless liquid, easily purified by chromatography on silica gel.⁸



Pure, neat **4** slowly decomposes or polymerizes at room temperature but is completely stable when stored as a 20% solution in hexane at 0 °C. The structure of cyclohexyne **4** was initially deduced from its mass (calcd for C₁₀H₂₄Si₄ *m/z* 256.09522, found *m/z* 256.09561), ¹H NMR (two singlets; δ 0.224, 0.175), ¹³C NMR, and ²⁹Si NMR spectra. The ¹³C NMR and ²⁹Si NMR spectral data for permethylhexasilacyclooctyne (**5**),⁷ **2**, and **4** are tabulated for comparison in Table I. As anticipated, the most dramatic effect is observed in ¹³C NMR absorption of the acetylenic carbons, which steadily shifts downfield to the remarkable value of δ 135.7 for **4**. This corresponds to a downfield shift of ca. 23 ppm from the acetylenic resonance of Me₃SiC≡SiMe₃.

Repeated attempts to obtain crystalline **4** were unsuccessful even at low temperatures. Thus, to obtain X-ray structural data

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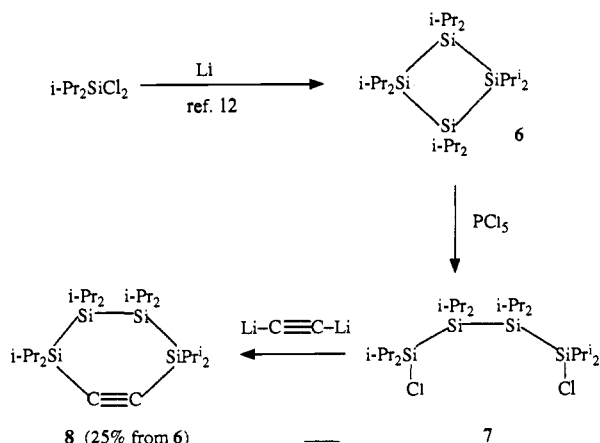
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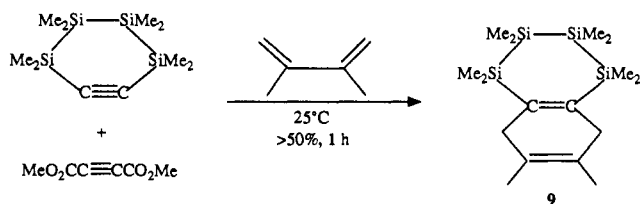
(10) Ando, W.; Hojo, F.; Sekigawa, S.; Nakayama, N.; Shimizu, T. *Organometallics* **1992**, *11*, 1009.

it was necessary to synthesize the more bulky derivative **8**. Synthesis of **8**¹¹ (colorless crystals, mp 67–68 °C) was accomplished by PCl₅-induced ring opening of cyclotetrasilane **6**¹² followed by condensation of the resulting 1,4-dichlorotetrasilane **7** with LiC≡CLi in 25% yield from **6**.



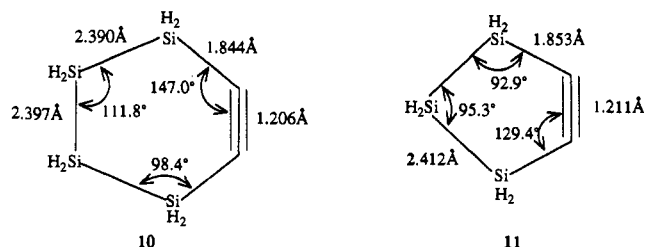
The crystal structure was solved by direct methods,¹³ and the molecular structure of **8** is shown in Figure 1. Crystal packing of **8** produces a molecular asymmetry which affords Si—C≡C bond angles of 146.8° and 150.5°. The smaller bond angle of 146.8° may be compared with the C—C≡C angle of cyclooctyne,¹⁴ 158.5°, and the smallest angle, 145.8 ± 0.7°, measured in 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne.⁴

The strain of the tetrasilacyclohexyne ring is clearly evidenced by enhanced chemical reactivity. For example, in a competition for a Diels–Alder Reaction with 2,3-dimethylbutadiene at room temperature, after 1 h, >50% of **4** had reacted to produce adduct **9**, while no detectable reaction of dimethyl acetylenedicarboxylate was observed.

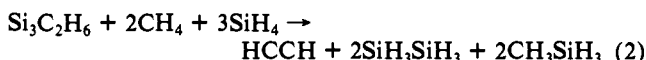
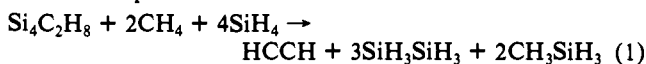


The structures of tetrasilacyclohexyne (**10**) and trisilacyclopentyne (**11**) were optimized with the 6-31G(d)¹⁵ basis set at the SCF level and verified as minima by diagonalizing the matrices of energy second derivatives (Hessians). The calculated and experimental structures for **10** agree quite well. The calculated SiCC angle of 147.0° compares well with an average experimental angle of 148.6°, although the angles in the crystal are clearly distorted by crystal packing. Ring contraction to trisilacyclopentyne (**11**) produces a dramatic reduction in the SiCC angle to 129.4°, making **11** a potentially isolable analog of benzyne.

To evaluate the stabilities of **10** and **11** the energies of the corresponding bond separation reactions¹⁶ were determined with



second-order perturbation theory (MP2)¹⁷ and the same basis set. The bond separation reactions are



The MP2/6-31G(d) enthalpies for the isodesmic reactions 1 and 2 are respectively +18.0 and –3.1 kcal/mol. Thus any strain introduced into the acetylenic moiety by placing it into the cyclic environment of **10** is more than offset by some delocalization into the silicon backbone. The greater strain in the five-membered ring of **11** decreases this stability by more than 20 kcal/mol. Although ring contraction of silacycloalkynes by thermal extrusion of silylenes is well-known through the work of Sakurai,¹⁸ our preliminary studies of the gas-phase pyrolysis of **4** have revealed no evidence of ring contraction to hexamethyltrisilacyclopentyne, although Me₂Si: is produced and trapped.

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Neighboring Tin Effect in Electron Transfer from Thioethers

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The neighboring silyl substituents in α -silyl ethers are known to significantly decrease the electrochemical oxidation potential of ethers,^{1–3} but not thioethers.^{3–5} Neighboring stannyl substituents with appropriate geometry in α -stannyl thioethers are now shown in this paper to dramatically render the anodic peak potential of the representative thioether 1,3-dithiane less positive.

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