

Macrocycles with Regularly Arranged Si–Si Bonds: Ring-Enlargement Oligomerization of Cyclic Disilanes via Palladium-Catalyzed Si–Si σ -Bond Metathesis

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A variety of organic macrocycles containing heteroatoms and functional groups have been synthesized and studied, demonstrating their novel chemical properties as functional molecules.¹ Proper arrangement of the group 14 elements in these organic macrocycles may possibly lead to the development of new functional molecules. In view of the interesting chemical and physical properties of Si–Si σ -bonds,² synthesis of macrocycles containing Si–Si σ -bonds in a regular arrangement may be an intriguing subject.

Recently, we have reported that bis(*tert*-butyl isocyanide)-palladium(0) (**1**) catalyzes a selective intramolecular Si–Si σ -bond metathesis of some bis(disilanyl)methanes.³ The use of *tert*-alkyl isocyanide ligand on palladium was crucially important for the activation of the Si–Si bonds.⁴ In this communication, we describe that a catalytic amount of **1** induces an oligomerization of 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**2**) through Si–Si σ -bond metathesis to give cyclic oligomers up to the 40-membered octamer. The present oligomerization is formally an insertion of a $-\text{Me}_2\text{Si}(\text{CH}_2)_3\text{SiMe}_2-$ unit of **2** into the Si–Si bonds of oligomers produced.

The cyclic disilane **2** (1.0 mmol) was stirred with benzene at 50 °C for 90 h in the presence of a catalytic amount of Pd(CNBu-*t*)₂ (**1**). The ¹H NMR spectrum of the reaction mixture showed clean conversion to oligomers **3**, which were subjected to preparative gel permeation chromatography to separate and isolate the cyclic dimer ($n = 2$, 3%), trimer ($n = 3$, 32%), tetramer ($n = 4$, 34%), pentamer ($n = 5$, 14%), hexamer ($n = 6$, 6%), heptamer ($n = 7$, 3%), and octamer ($n = 8$, 1%) (93% in total, Scheme 1). The cyclic structure of the tetramer was established by single-crystal X-ray diffraction, which indicated that the four Si–Si bonds in the ring were in a nearly parallel arrangement (Figure 1).⁵

The oligomerization proceeded smoothly until **2** was completely consumed, and it did not lead to high molecular weight

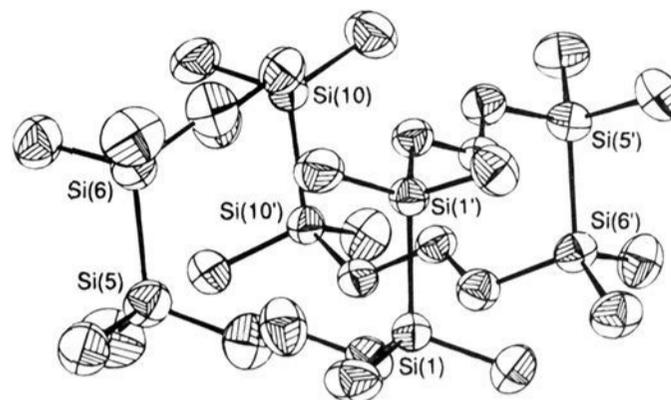
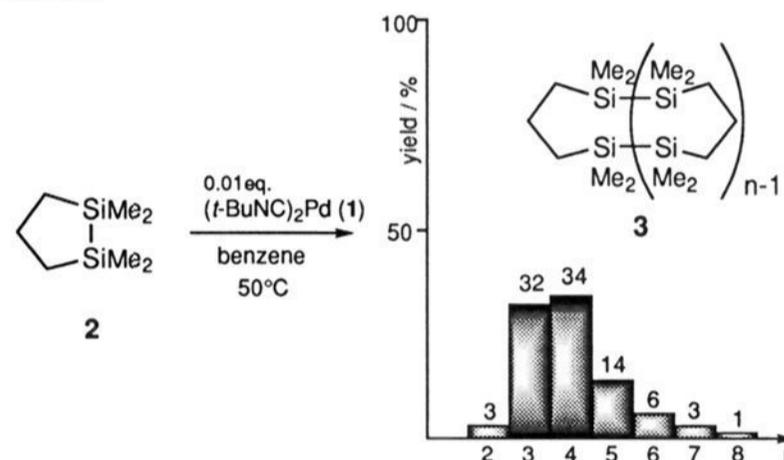
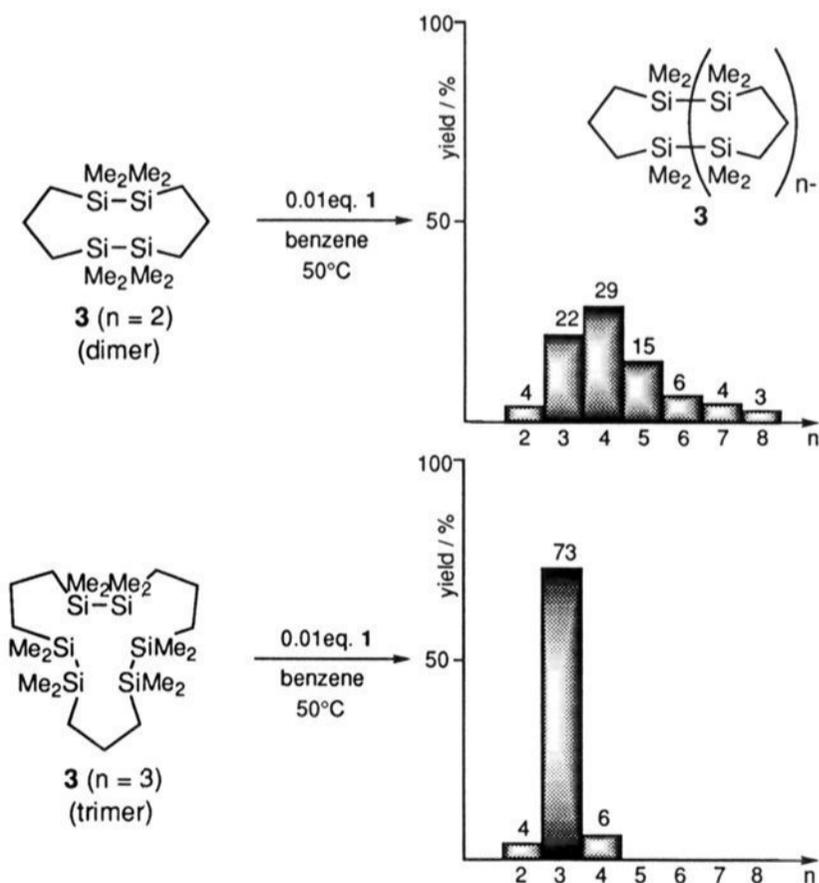


Figure 1. Crystal structure of tetramer **3** ($n = 4$). Hydrogen atoms were omitted for clarity.

Scheme 1



Scheme 2. Reactions of Isolated Oligomers **3** ($n = 2, 3$) in the Presence of Pd(CNBu-*t*)₂ (**1**)



polymer. Treatment of each isolated oligomer ($n = 2, 3$, and 4) under the reaction conditions revealed that the present Si–Si σ -bond metathesis was reversible (Scheme 2). Thus, the reaction starting with the 10-membered cyclic dimer ($n = 2$) afforded a mixture of oligomers in an almost identical distribution to that of the reaction with **2**. Deoligomerization of the dimer followed by oligomerization of the resultant **2** may be presumed. The cyclic trimer ($n = 3$) and tetramer ($n = 4$) underwent the deoligomerization and oligomerization only to the $(n-1)$ mer and $(n+1)$ mer, respectively, to a lesser extent. These findings imply that the oligomerization did not proceed by σ -bond metathesis between two oligomers but between the five-membered cyclic disilane **2** and the oligomer. A schematic

(1) Vögtle, F. *Supramolecular Chemistry*; John Wiley & Sons: Chichester, 1991; pp 9–128 and references therein.

(2) (a) West, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, 1989; Chapter 19. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359–1410. (c) Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 419–421 and references therein.

(3) Suginome, M.; Oike, H.; Ito, Y. *Organometallics* **1994**, *13*, 4148–4150.

(4) (a) Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948–1951. (b) Murakami, M.; Suginome, M.; Fujimoto, K.; Nakamura, H.; Andersson, P. G.; Ito, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6487–6498. (c) Murakami, M.; Suginome, M.; Fujimoto, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1473–1475 and references therein.

(5) Crystal data for the tetramer: crystal size $0.50 \times 0.50 \times 0.30$ mm (recrystallized from CHCl_3); monoclinic, space group $C2/c$ (No. 15), $Z = 4$; $a = 21.700(8)$ Å, $b = 13.598(6)$ Å, $c = 15.336(9)$ Å; $\beta = 107.88(4)^\circ$; $V = 4307(3)$ Å³, $\rho_{\text{calcd}} = 0.98$ g/cm³; maximum $2\theta = 50^\circ$ (Mo $K\alpha$ $\lambda = 0.71073$ Å, graphite monochromator, $\omega/2\theta$ scan, $T = 293$ K); 5432 reflections measured, 4953 independent, 3417 included in the refinement, Lorentzian polarization and absorption corrections by analytical function ($\mu = 2.27$ cm⁻¹); direct method, anisotropic refinement for non-hydrogen atoms by full-matrix least squares against $|F^2|$ with program package CrystanG (Mac Science), 277 parameters; $R = 0.065$, $R_w = 0.071$; residual electron density $0.86/-0.65$ e/Å³. All hydrogen atoms were located on a difference electron density map and refined with isotropic thermal parameters calculated from those of the bonded atoms.

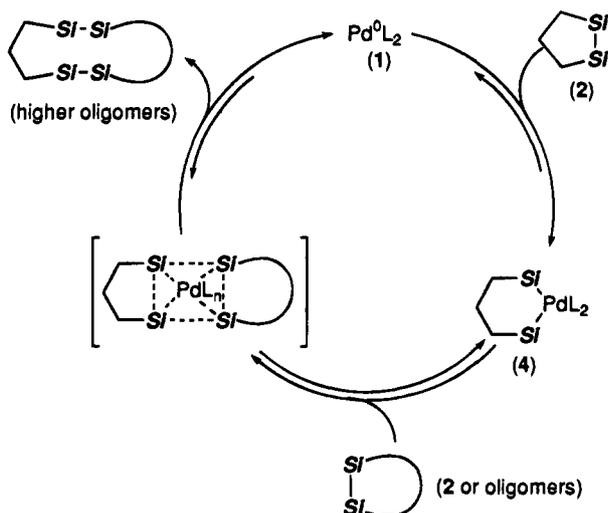
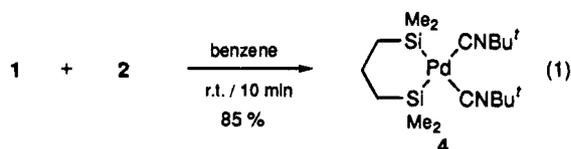
Scheme 3. Possible Mechanism for Si-Si σ -Bond Metathesis Oligomerization

illustration is presented for the ring-enlargement oligomerization of **2** as follows (Scheme 3).

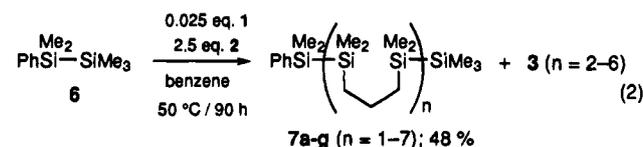
Oxidative addition of **2** onto Pd(CNBu-*t*)₂ (**1**) affords six-membered bis(silyl)palladium complex **4**, which may react with the Si-Si bond of **2** or the oligomers via five-centered activation,³ to give higher cyclic oligomers. In fact, intermediate **4**, which was immediately formed in the stoichiometric reaction of **2** with **1**, was isolated in 85% yield as thermally stable but air-sensitive crystals (eq 1).⁶ In contrast, six-membered 1,1,2,2-tetramethyldisilacyclohexane (**5**) did not react with **1**. Consequently, no oligomerization of **5** took place at all.



The mechanism, in which the -Me₂Si(CH₂)₃SiMe₂- unit of **2** was successively inserted into the Si-Si bond, was also supported by the fact that phenylpentamethyldisilane (**6**) underwent insertion of **2** to give acyclic products **7a-g** ($n =$

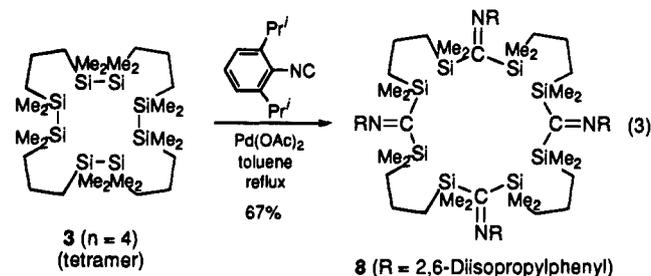
(6) **3**: mp 79–81 °C dec; ¹H NMR (C₆D₆) δ 0.83 (s, 12 H), 1.00 (s, 18 H), 1.24–1.33 (m, 4 H), 2.47–2.51 (m, 2 H); ¹³C NMR (C₆D₆) δ 7.1, 22.3, 22.8, 29.7, 55.8, 147.5; IR (C₆H₆) 2168, 2148 cm⁻¹. Anal. Calcd for C₁₇H₃₆N₂PdSi₂: C, 47.37; H, 8.42; N, 6.50. Found: C, 47.14; H, 8.59; N, 6.38.

1–7)⁷ in 48% yield (based on starting **6**) along with the cyclic oligomers **3** derived from **2** (eq 2).



It is noted, however, that, in the presence of the Pd(C₅H₅)-(C₃H₅) catalyst, the five-membered disilane **2** afforded polymers with very high molecular weights (51%, Mn > 500 000) along with the cyclic dimer (37%). No other oligomers were found. A similar result has been reported by Suzuki et al., who carried out the reaction of **2** in the presence of Pd₂(dba)₃CHCl₃ with PPh₃ in CH₃CN.⁸ The mechanistic difference remains to be clarified.⁹

The cyclic molecules thus far prepared, which contain Si-Si linkages in the ring, are further elaborated by virtue of the high but controllable reactivities of Si-Si toward transition metal complex catalysts, as demonstrated by isocyanide insertion into all the Si-Si bonds of the 20-membered cyclic tetramer (eq 3).¹⁰



Supplementary Material Available: Detailed experimental procedures, characterization of new compounds, and tables of final atomic coordinates, thermal parameters, bond distances, and bond angles for the tetramer (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(7) **7a** ($n = 1$, 20%), **7b** ($n = 2$, 13%), **7c** ($n = 3$, 8%), **7d** ($n = 4$, 5%), **7e** ($n = 5$, 2%), **7f** ($n = 6$, 1%), and **7g** ($n = 7$, 0.6%) were isolated.

(8) Suzuki, M.; Obayashi, T.; Amii, H.; Saegusa, T. *Polym. Prep. Jpn.* **1991**, *40*, 355.

(9) (a) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19–21. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1977**, *131*, 147–152. (c) Kusukawa, T.; Kabe, Y.; Ando, W. *Chem. Lett.* **1993**, 985–988.

(10) Ito, Y.; Sugimoto, M.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1991**, *113*, 8899–8908.