# Isolation and Molecular Structure of Persilylated [5]Radialene: Intramolecular Cyclization of a Macrocyclic Pentayne with $Mn(CO)_3(Me\text{-}Cp)$

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Persilyl-substituted [5]radialene (**2**) was isolated as orange crystals by the intramolecular cyclization of 3,3,6,6,8,8,11,11,14,14,16,16,19,19,21,21-hexadecamethyl-3,6,8,11,14,16,19,21-octasilacyclohenicosa-1,4,9,12,17-pentayne (**1**) with an excess molar amount of $[Mn(CO)_3(Me\text{-}Cp)]$ by irradiation ($\lambda >$ 300 nm) under reflux in THF. The molecular structure and properties of the persilylated [5]radialene **2** are described.

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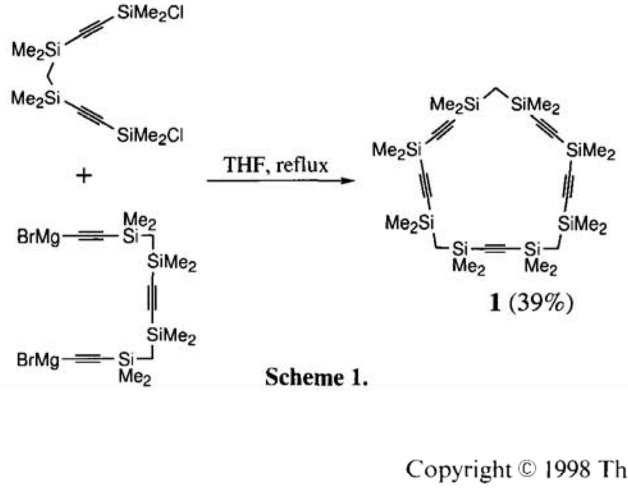
Radialene has received considerable attention because of its special arrangement of π-electrons. Various radialene derivatives have been reported so far, but the synthetic methods are very limited. In particular, there are only a few reports on the synthesis of [5]radialene (pentamethylenecyclopentane) derivatives with a ten π-electron system.[1] In previous studies, we have demonstrated the intramolecular cyclooligomerization of the silacyclotriynes with transition metal complexes to give a variety of persilyl-substituted π-electron systems, such as dimethylenecyclobutene derivatives.[2] More recently, we have reported that the silacyclotetrayne underwent intramolecular cyclization with $[Mn(CO)_3(Me\text{-}Cp)]$ to form persilylated [4]radialene and trimethylenecyclopentene derivatives with an eight π-electron system.[3] All of these reactions involve a 1,2-silyl shift in the 1,2-disilyl-substituted acetylene to give 2,2-disilylvinylidene complexes as a key reaction intermediate. In this paper, we wish to report the one-pot synthesis of persilyl-substituted [5]radialene, an interesting extension of the intramolecular cyclization to a macrocyclic pentayne linked by tetramethyldisilmethylene ($Me_2SiCH_2SiMe_2$) and dimethylsilylene ($SiMe_2$) chains.

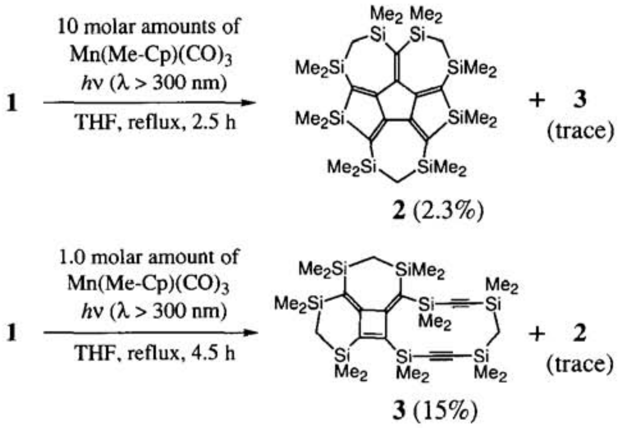
The precursor of 3,3,6,6,8,8,11,11,14,14,16,16,19,19,21,21-hexadecamethyl-3,6,8,11,14,16,19,21-octasilacyclohenicosa-1,4,9,12,17-pentayne (**1**) was prepared by the coupling reaction of 2,10-dichloro-2,5,5,7,7,10-hexamethyl-2,5,7,10-tetrasilaundeca-3,8-diyne with the Grignard reagent prepared from 3,3,5,5,8,8,10,10-octamethyl-3,5,8,10-tetrasiladodeca-1,6,11-triyne and ethylmagnesium bromide in 39% yield (Scheme 1).[4]



**1** (39%)

**Scheme 1.**

A mixture of the macrocyclic pentayne **1** (400 mg, 0.64 mmol) and a large excess molar amount of $[Mn(CO)_3(Me\text{-}Cp)]$ (1396 mg, 6.40 mmol) in THF (35 ml) was irradiated with a 500 W high-pressure mercury lamp at the refluxing temperature of THF to produce orange crystals of the persilylated [5]radialene derivative (**2**) in 2.3% yield (9.1 mg, 0.015 mmol) (Scheme 2). The reaction mechanism remains unclear. Nevertheless, a quintuple 1,2-silyl shift must be involved for the formation of **2**. The 1,2-silyl shift was accelerated by heat, and none of the radialene derivative was formed in the reaction at room temperature. However, the use of an equimolar amount of the manganese complex resulted in the formation of the dimethylenecyclobutene derivative (**3**) as pale yellow crystals in 15% yield. Compounds **2** and **3** were fully characterized by NMR spectroscopy.[5,6] The dimethylenecyclobutene **3** was not a precursor of **2** since **3** did not afford **2** under the reaction conditions. Therefore, the products **2** and **3** are derived from different reaction pathway. The high reaction temperature and a large excess of the manganese complex, which promote the intriguing 1,2-silyl shift, are crucial for the synthesis of the persilylated [5]radialene **2**. The same results were obtained by using $[Mn(CO)_3(Cp)]$.



**Scheme 2.**

Oligomerization of acetylene, catalyzed by transition metal complexes, is a very important class of reactions that lead to benzene as a trimer and cyclooctatetraene as a tetramer.[7] Although the yield is low, the persilylated [5]radialene **2** is the first example of the cyclopentamerization of acetylene units.

NMR data of **2** shows a symmetric structure in solution on the NMR time scale. Thus, in the $^1H$ NMR spectrum of **2**, four sets of methyl groups and two sets of methylene groups were found. In the $^{29}$Si NMR spectrum, four sets of signals were observed at −12.0, −10.0, −8.4, and 30.9 ppm. The $^{29}$Si NMR signal in a silacycle has been reported at lower field than for similar acyclic compounds.[8] Thus, the $^{29}$Si NMR signal appearing at 30.9 ppm can be assigned to the silicon of the silacyclopentadiene moiety of **2**. In the $^{13}$C NMR spectrum, six sets of quaternary carbon atoms were found at 143.3, 144.9, 157.0, 163.2, 164.7, and 172.0 ppm. In the UV-visible spectrum of **2**, three absorption bands at $\lambda_{max}$/nm (ε) 264 (44600), 379 (2800), 428 (2700) were observed. The latter absorption band tails into the visible region until about 500 nm.

The molecular structure of **2** was unambiguously determined by X-ray crystallography.[9] An ORTEP drawing of **2** is shown in Figure 1. The persilylated [5]radialene **2** possesses a unique 10 π-electron system; five double bonds are located at the exo position. Only one example of the crystal structure of a permethyl-substituted[5]radialene is known.[1a] The persilylated [5]radialene **2** has a distorted structure and the central five-membered ring is not planar, but has an envelope conformation. The angle formed by C2–C3–C4-C5 and C1–C2–C5 planes is 19.0(0)°. The internal bond angles of the central five-membered ring are 104.8(2) – 110.3(2)° (av 107.2°), and sum of the bond angles is 536.1°. In contrast, the two silole (silacyclopentadiene) rings have an almost planar structure. The appreciable bond alternation between the single and double bonds of the π-skeleton of **2** is a characteristically structural feature of a cross-conjugated diene. The average lengths of C–C single and double bonds are 1.501(4) and 1.365(4) Å, respectively.

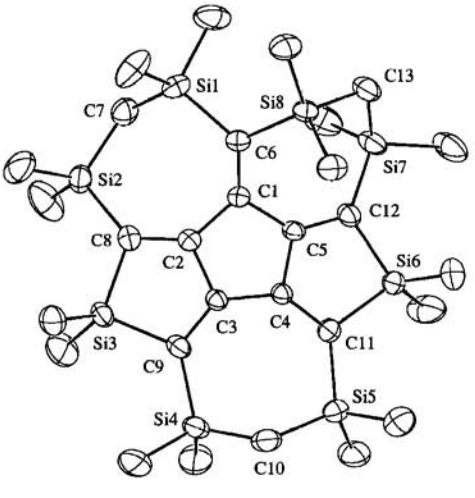


**Figure 1.** ORTEP drawing of **2** (hydrogen atoms are omitted for the clarity).

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## References and Notes

1 a) M. Iyoda, H. Otani, M. Oda, Y. Kai, Y. Baba, and N. Kasai, *J. Chem. Soc., Chem. Commun.*, **1986**, 1794. b) Z. Yoshida and T. Sugimoto, *Angew. Chem., Int. Ed. Engl.*, **27**, 1573 (1988). c) K. Kano, T. Sugimoto, Y. Misaki, T. Enoki, H. Hatakeyama, H. Oka, Y. Hosotani, and Z. Yoshida, *J. Phys. Chem.*, **98**, 252 (1994).

2 K. Ebata, T. Matsuo, T. Inoue, Y. Otsuka, C. Kabuto, A. Sekiguchi, and H. Sakurai, *Chem. Lett.*, **1996**, 1053.

3 a) A. Sekiguchi, T. Matsuo, and C. Kabuto, *Angew. Chem., Int. Ed. Engl.*, **36**, 2462 (1997). b) A. Sekiguchi, T. Matsuo, and R. Akaba, *Bull. Chem. Soc. Jpn.*, **71**, 41 (1998). c) A. Sekiguchi, T. Matsuo, and H. Sakurai, *Angew. Chem., Int. Ed. Engl.*, **37**, 1661 (1998). d) T. Matsuo, A. Sekiguchi, M. Ichinohe, K. Ebata, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **71**, 1705 (1998).

4 Spectral data for **1**: colorless crystals, mp 68 – 69 °C; $^1$H NMR (CDCl$_3$, δ) 0.00 (s, 4 H, CH$_2$), 0.03 (s, 2 H, CH$_2$), 0.22 (s, 12 H, CH$_3$), 0.25 (s, 24 H, CH$_3$), 0.28 (s, 12 H, CH$_3$); $^{13}$C NMR (CDCl$_3$, δ) 0.1 (CH$_3$), 0.9 (CH$_3$ x 2), 1.0 (CH$_3$), 3.2 (CH$_2$ x 2), 110.1 (C), 110.2 (C), 114.8 (C), 115.7 (C x 2); $^{29}$Si NMR (CDCl$_3$, δ) −42.7, −19.6, −18.9, −18.8; UV (hexane) $\lambda_{max}$/nm (ε) 209 (5800), 218 (3900).

5 Spectral data for **2**: orange crystals, mp 140 – 142 °C; $^1$H NMR (CDCl$_3$, δ) 0.10 (s, 2 H, CH$_2$), 0.13 (s, 12 H, CH$_3$), 0.14 (s, 12 H, CH$_3$), 0.15 (s, 12 H, CH$_3$), 0.286 (s, 12 H, CH$_3$), 0.290 (s, 4 H, CH$_2$); $^{13}$C NMR (CDCl$_3$, δ) −2.3 (CH$_3$), 1.1 (CH$_3$), 1.5 (CH$_3$), 3.0 (CH$_3$), 4.9 (CH$_2$), 11.7 (CH$_2$), 143.3 (C), 144.9 (C), 157.0 (C), 163.2 (C), 164.7 (C), 172.0 (C); $^{29}$Si NMR (CDCl$_3$, δ) −12.0, −10.0, −8.4, 30.9; UV $\lambda_{max}$/nm (ε) 264 (44600), 379 (2800), 428 (2700). Found: C, 55.28; H, 8.68%. Calcd for $C_{29}H_{54}Si_8$: C, 55.52; H, 8.67%.

6 Spectral data for **3**: pale yellow crystals, mp 130 – 131 °C; $^1$H NMR (CDCl$_3$, δ) −0.17 (s, 2 H, CH$_2$), −0.16 (s, 2 H, CH$_2$), 0.01 (s, 2 H, CH$_2$), 0.13 (s, 6 H, CH$_3$), 0.15 (s, 6 H, CH$_3$), 0.17 (s, 6 H, CH$_3$), 0.18 (s, 6 H, CH$_3$), 0.22 (s, 6 H, CH$_3$), 0.31 (s, 6 H, CH$_3$), 0.38 (s, 6 H, CH$_3$), 0.41 (s, 6 H, CH$_3$); $^{13}$C NMR (CDCl$_3$, δ) 0.9 (CH$_3$), 1.1 (CH$_2$), 1.2 (CH$_3$), 1.7 (CH$_3$), 1.8 (CH$_2$), 2.7 (CH$_3$), 2.8 (CH$_3$), 3.2 (CH$_3$), 3.6 (CH$_3$), 3.7 (CH$_3$), 7.6 (CH$_2$), 114.5 (C), 116.1 (C x 2), 116.5 (C), 119.6 (C), 121.5 (C), 172.6 (C), 173.0 (C), 176.4 (C), 184.2 (C); $^{29}$Si NMR(CDCl$_3$, δ) −33.7, −28.6, −19.3, −19.2, −16.5, −7.6, −6.8, −6.3; UV $\lambda_{max}$/nm (ε) 250 (26500), 280 (sh. 9600), 324 (sh. 5100). Found: C, 55.44; H, 8.92%. Calcd for $C_{29}H_{54}Si_8$: C, 55.52; H, 8.67%.

7 a) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann. Chem.*, **560**, 1 (1948); b) W. Reppe and W. J. Schweckendiek, *Ann. Chem.*, **560**, 104 (1948).

8 J. Dubac, A. Laporterie, and G. Manuel, *Chem. Rev.*, **90**, 215 (1990).

9 Crystal data for **2**: MF = $C_{29}H_{54}Si_8$, MW = 627.44, monoclinic, a = 12.831(1), b = 14.975(1), c = 19.943(1) Å, β = 93.902(3)°, $V$ = 3823.0(2) Å$^3$, space group = $P2_1/n$, Z = 4, $D_{calcd}$ = 1.090 g cm$^{-3}$. The final $R$ factor was 0.046 ($R_w$ = 0.048) for 6750 reflections with $I > 3\sigma(I)$. Selected bond lengths (Å) and bond angles (deg.): C1–C2 1.506(4), C1–C5 1.485(4), C1–C6 1.375(4), C2–C3 1.528(4), C2–C8 1.362(4), C3–C4 1.483(4), C3–C9 1.363(4), C4–C5 1.502(4), C4–C11 1.363(4), C5–C12 1.363(4), C2–C1–C5 104.8(2), C2–C1–C6 130.5(3), C5–C1–C6 123.7(3), C1–C2–C3 107.0(2), C1–C2–C8 136.0(3), C3–C2–C8 116.9(3), C2–C3–C4 108.2(2), C2–C3–C9 117.6(3), C4–C3–C9 133.9(3), C3–C4–C5 105.8(2), C3–C4–C11 136.5(3), C5–C4–C11 117.5(3), C1–C5–C4 110.3(2), C1–C5–C12 131.3(3), C4–C5–C12 118.2(3).