Intramolecular Oligomerization of Disilalkylene {-$Me_2Si(CH_2)_nSiMe_2$-} Bridged Cyclic Triacetylenes[1]

Keisuke Ebata,† Tsukasa Matsuo, Tsuyotoshi Inoue, Yuko Otsuka, Chizuko Kabuto, Akira Sekiguchi, and Hideki Sakurai*††
Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai, Miyagi 980-77
†NTT Basic Research Laboratories, Morinosato Wakamiya 3-1, Atsugi, Kanagawa 243-01
††Department of Industrial Chemistry, Faculty of Science, Science University of Tokyo, Noda, Chiba 277

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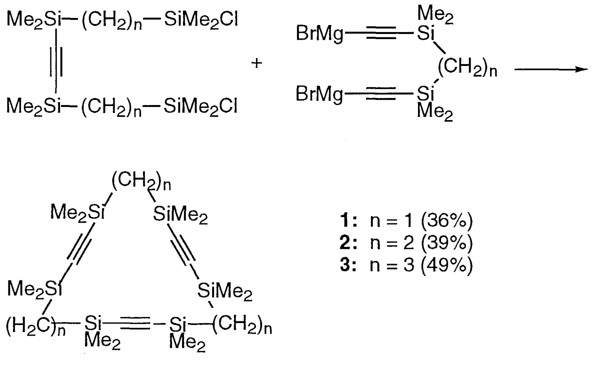
Disilalkylene bridged cyclic triacetylenes are prepared and subjected to the transition metal complex mediated reactions. In particular, the reaction with (methylcyclopentadienyl)tricarbonylmanganese gave a variety of π-electron systems such as fulvene, dimethylenecyclobutene, and biallene. Structures and reactions of these π-electron systems are described.

Oligomerization of acetylene, catalyzed by transition-metal complexes, is an interesting class of reactions to lead to benzene as a trimer and cyclooctatetraene as a tetramer.[2] In previous studies, we have demonstrated that macrocyclic polyacetylenes tethered by disiloxane bridges (-$SiMe_2$-O-$SiMe_2$-) undergo intramolecular cyclization to a variety of π electron systems,[3] where a vinylidene complex was isolated as an intermediate.[4] More recently, it is demonstrated that not only cyclic but acyclic acetylenes substituted by two silyl groups on each end undergo facile 1,2-silyl shift in the reaction with (cyclopentadienyl)tricarbonylmanganese under photochemical conditions to give 2,2-disilylvinylidene complexes.[5]

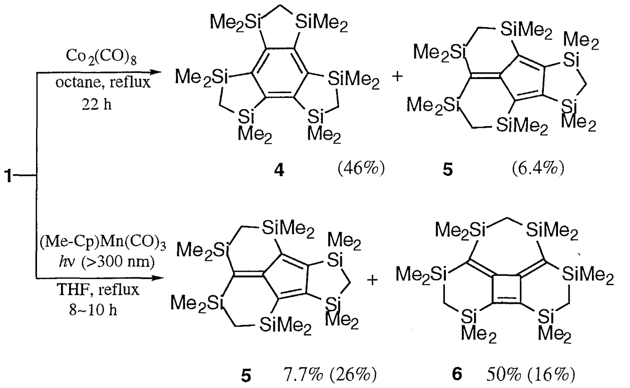
In this paper, we report an interesting extension of these reactions to macrocyclic polyacetylenes tethered by disilalkylene {-$SiMe_2$-$(CH_2)_n$-$SiMe_2$-} instead of disiloxane bridges. Since the disilmethylene and other disilalkylene bridges are more rigid than the disiloxane, multiple 1,2-silyl shift may be expected during the reaction to new products involving novel reaction modes.

Preparation of the disilalkylene-bridged cyclic triacetylenes (**1** - **3**) is rather straightforward by the coupling reactions of the respective dichlorosilanes with bis(ethynyl) Grignard reagents in fair to good yields.



1: n = 1 (36%)
2: n = 2 (39%)
3: n = 3 (49%)

First, intramolecular trimerization of the cyclic triacetylene **1** was examined. The reaction catalyzed by octacarbonyldicobalt gave mainly a benzene derivative (**4**) but the reaction in the presence of 1.0 eq. of (Me-Cp)$Mn(CO)_3$ under irradiation with a super high-pressure mercury arc lamp with a filter (>300 nm) afforded fulvene (**5**) and dimethylenecyclobutene (**6**) derivatives.[6] This is the first example of the formation of dimethylenecyclobutene by trimerization of acetylenes in which double 1,2-silyl shift is required. Compounds **5** and **6**, obtained as red and pale yellow crystals, respectively, are very stable and fully characterized by NMR.[7,8] Interestingly in the latter reaction, the yield of dimethylenecyclobutene **6** increased by increasing temperature and *vice versa* for fulvene **5**. (Yields in parentheses are those at room temperature). Apparently, the second 1,2-silyl shift requires higher activation energy.



Me-Cp = methylcyclopentadienyl

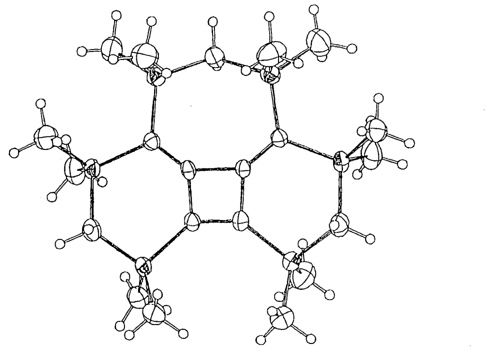
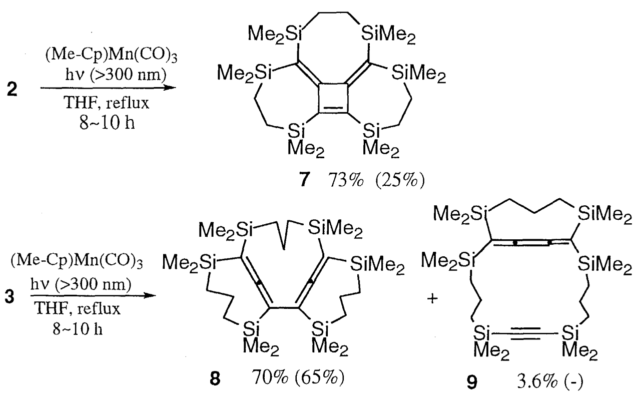


Figure 1. ORTEP drawing of **6**.

The molecular structure of **6** was also determined by the X-ray crystallographic method.[9] An ORTEP drawing of **6** is shown in Figure 1. Only one example of highly distorted 1,2-di-*t*-butyl-3,4-diisopropyllidene-1-cyclobutene has been reported so far as the structure of 3,4-dimethylenecyclobutene.[10] Although the latter is strongly folded due to the steric compression, the cyclobutene ring of **6** is almost planar.

Irradiation of a hexane solution of **6** with a super high-pressure mercury arc lamp without a filter resulted in the formation of **5** in 12% yield. Although photochemical yield is low, the reaction is a quite unique class of isomerization since it should involve both reverse 1,2-silyl shift and ring enlargement.



7 73% (25%)

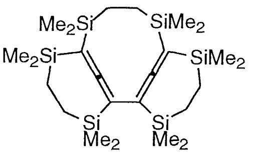
8 70% (65%)

9 3.6% (-)

Cyclic triacetylenes with larger tethers, *i.e.* disilethylene- (**2**) and disilpropylene-bridged (**3**) compounds are also subjected to the Mn-complex catalyzed reaction. The compound **2** gave a dimethylenecyclobutene (**7**) similarly.[11]

At higher temperature, **7** was obtained preferably in high yield. Yields in parentheses also indicate those at room temperature. However, the compound **3** did not give dimethylenecyclobutene any more. Instead, a biallene compound (**8**)[12] and a small amount of butatriene-yne (**9**)[13] are obtained. Apparently, a fused ring system, composed of 4-, 8-, and 9-membered rings as expected for the formation of dimethylenecyclobutene, is very much strained to cause facile rupture of the cyclobutene ring in two ways.

Dimethylenecyclobutene **7** also undergoes similar ring rupture by thermolysis to give **10** and upon irradiation to **11**. Difference in the mode of isomerization by photolysis and thermolysis is interesting but the reason is not clear at this moment.



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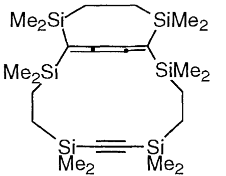

11

Persilyl-substituted π electron systems can be readily reduced with lithium to dianions. Tetrakis(trimethylsilyl)ethylene and silylbenzenes form dianions whose structures have been determined recently.[14,15]

Dimethylenecyclobutene **6** can also be reduced with lithium metal in DME to give a solution of the dianions. These dianions were isolated as air-sensitive lithium complexes. Details will be reported soon.

References and Notes

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4 H. Sakurai, K. Hirama, Y. Nakadaira, and C. Kabuto, *J. Am. Chem. Soc.*, **109**, 6880 (1987).

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6 Spectral data for **4**: colorless crystals, mp 219 - 220 °C; ^{1}H NMR ($CDCl_3$) δ -0.14 (s, 6H), 0.39 (s, 36H); ^{13}C NMR ($CDCl_3$) δ 0.7, 3.8, 156.0; ^{29}Si NMR ($CDCl_3$) δ 6.8; HRMS m/z Calcd for $C_{21}H_{42}Si_6$ 462.1902, Found 462.1905.

7 Spectral data for **5**: red crystals, mp 170 °C; ^{1}H NMR ($CDCl_3$) δ -0.12 (s, 4H), 0.29 (s, 2H), 0.30 (s, 12H), 0.34 (s, 12H), 0.41 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 1.8, 1.9, 3.2, 3.4, 3.5, 143.8, 167.1, 168.4, 182.9; ^{29}Si NMR ($CDCl_3$) δ -13.4, -6.7, -2.4; HRMS m/z Calcd for $C_{21}H_{42}Si_6$ 462.1902, Found 462.1894.

8 Spectral data for **6**: pale yellow crystals, mp 199 - 200 °C; ^{1}H NMR ($CDCl_3$) δ -0.13 (s, 4H), 0.01 (s, 2H), 0.15 (s, 12H), 0.18 (s, 12H), 0.20 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 0.39, 0.4, 2.7, 3.0, 7.4, 126.3, 173.5, 177.1; ^{29}Si NMR ($CDCl_3$) δ -17.5, -7.3, -7.1; HRMS m/z Calcd for $C_{21}H_{42}Si_6$ 462.1902, Found 462.1914.

9 Crystal data for **6**: MF = $C_{21}H_{42}Si_6$, MW = 463.08, monoclinic, a = 21.400(1), b = 10.761(1), c = 12.948(1) Å, β = 107.72(0)°, V = 2840.4(5) Å^3, space group = $P2_1/a$, Z = 4, D_{calcd} = 1.083 g cm^{-3}. The final R factor was 0.0733 (Rw = 0.0848) for 4094 reflections with Fo > 3σ(Fo). Selected bond lengths (Å) and bond angles (deg.): C1-C2 1.371(7), C2-C3 1.501(7), C3-C4 1.563(7), C4-C1 1.493(7), C3-C5 1.349(7), C4-C6 1.346(7); C2-C1-C4 94.2(4), C1-C2-C3 93.1(4), C2-C3-C4 86.5(3), C1-C4-C3 86.1(3), C2-C3-C5 133.0(5), C4-C3-C5 140.5(5), C1-C4-C6 132.9(5), C3-C4-C6 141.0(5)

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11 Spectral data for **7**: pale yellow crystals, mp 112 °C; ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 12H), 0.11 (s, 12H), 0.20 (s, 12H), 0.76 (s, 4H), 0.82 (s, 8H); ^{13}C NMR ($CDCl_3$) δ -0.2 ($SiMe_2$), 1.5 (2 x $SiMe_2$), 9.1, 11.3, 11.7, 115.2, 175.0, 179.1; ^{29}Si NMR ($CDCl_3$) δ -8.8, -3.9, -3.4; HRMS m/z Calcd for $C_{24}H_{48}Si_6$ 504.2372, Found 504.2365.

12 Spectral data for: **8**: colorless crystals, mp 133 - 134 °C; ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 6H), 0.07 (s, 6H), 0.08 (s, 6H), 0.09 (s, 12H), 0.13 (s, 6H), 0.48 - 0.69 (m, 6H), 0.70 - 0.85 (m, 4H), 0.98 - 1.10 (m, 2H), 1.60 - 1.80 (m, 6H) ; ^{13}C NMR ($CDCl_3$) δ -3.6, -2.3, -0.9, -0.8, -0.4, -0.2, 16.0, 16.7, 16.9, 17.9, 23.2, 69.8, 74.8, 207.8; ^{29}Si NMR ($CDCl_3$) δ -4.6, -4.1, -1.3; HRMS m/z Calcd for $C_{27}H_{54}Si_6$ 546.2841, Found m/z 546.2849..

13 Spectral data for **9**: orange crystals, mp 45 °C; ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 12H), 0.14 (s, 12H), 0.17 (s, 12H), 0.59 (m, 4H), 0.76 (m, 8H), 1.40 (m, 4H), 1.55 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -1.8, -1.7, 0.3, 18.5, 18.6, 19.6, 20.5, 20.8, 113.7, 154.8, 209.6; ^{29}Si NMR ($CDCl_3$) δ -17.9, -7.3, -6.7.

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