

Novel π -electron systems derived from silicon-containing macrocyclic polyacetylenes

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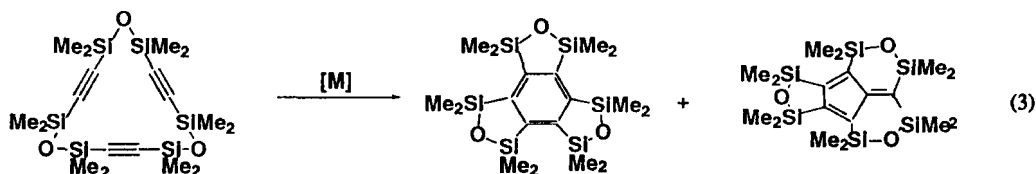
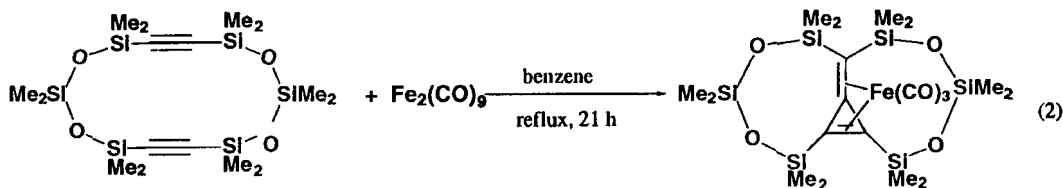
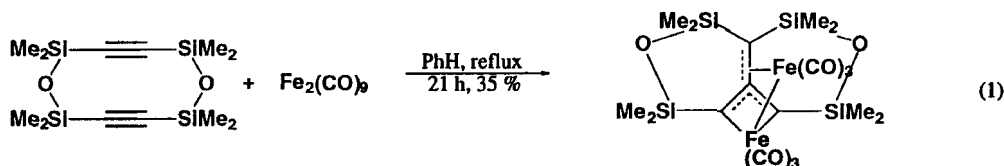
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Abstract:

Disilylmethylene bridged cyclic triacetylene and tetraacetylene are prepared and subjected to the transition metal complex mediated reactions. In particular, the reaction with (cyclopentadienyl)tricarbonylmanganese gave a variety of cross-conjugated systems such as fulvene, dimethylenecyclobutene, trimethylenecyclopentene and radialene. Structures and reactions of these interesting π -electron systems are described. Dianions derived from these systems are also discussed briefly.

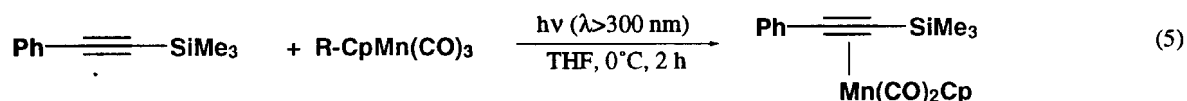
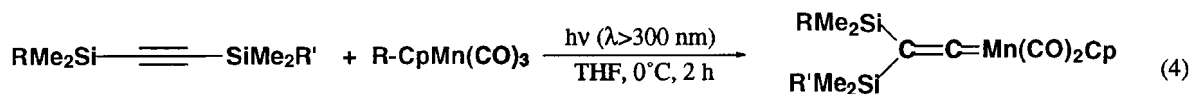
Introduction

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 (1). In previous studies, we have demonstrated that macrocyclic polyacetylenes tethered by disiloxane bridges (-SiMe₂-O-SiMe₂-) undergo interesting intramolecular cyclization to a variety of π electron systems (2).



The characteristic capacity of silicon to undergo 1,2-shift in disilylacetylenes is responsible for the formation of the unusual products shown above. The 1,2-silyl shift from 1,2-disilylacetylene should give 2,2-disilylvinyldiene complexes. The latter undergoes further transformation to give respective products under the conditions. A key intermediate in the cyclotrimerization has been isolated and the structure has been determined by the X-ray crystallographic method (3).

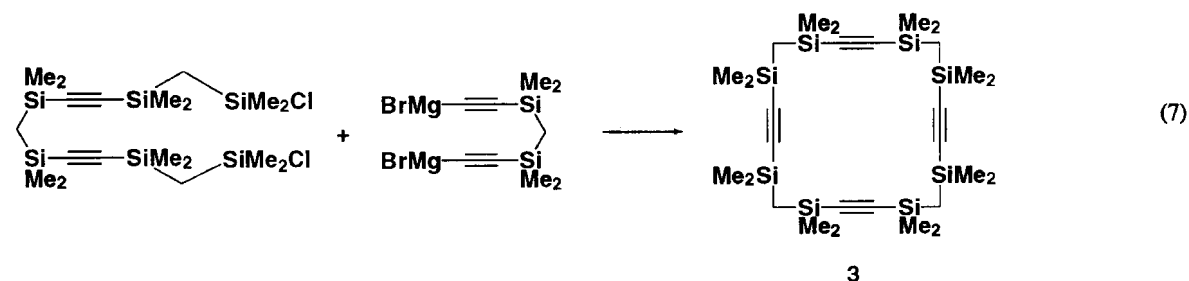
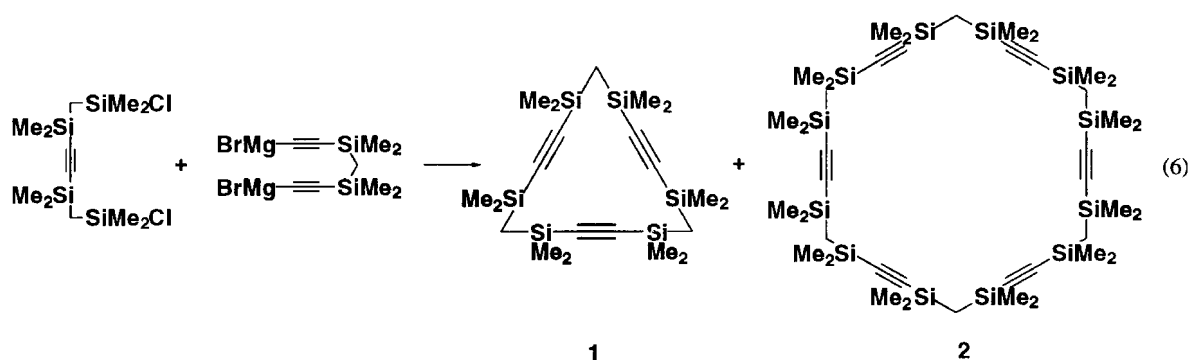
More recently, it has been demonstrated that not only cyclic but acyclic acetylenes substituted by two silyl groups on each end undergo facile 1,2-silyl shift in the reaction with (cyclopentadienyl)tricarbonylmanganese under photochemical conditions to give 2,2-disilylvinyldene complexes (4). Existence of two silyl groups on each terminal of acetylene is essential for the reaction at least under the conditions, because phenyl(trimethylsilyl)acetylene did not afford the corresponding vinyldene complexes, but an acetylene complex was obtained.



We have recently extended these reactions for macrocyclic polyacetylenes tethered by disilmethylene (-SiMe₂-CH₂-SiMe₂-) instead of disiloxane bridges. Since the disilmethylene bridge is more rigid than the disiloxane, multiple 1,2-silyl shift may be expected during the reaction and hence new products and novel reaction modes can be anticipated (5). Herein we report the latest results in this line of the chemistry. The chemistry of dianions produced by two electron reduction of these products are also described.

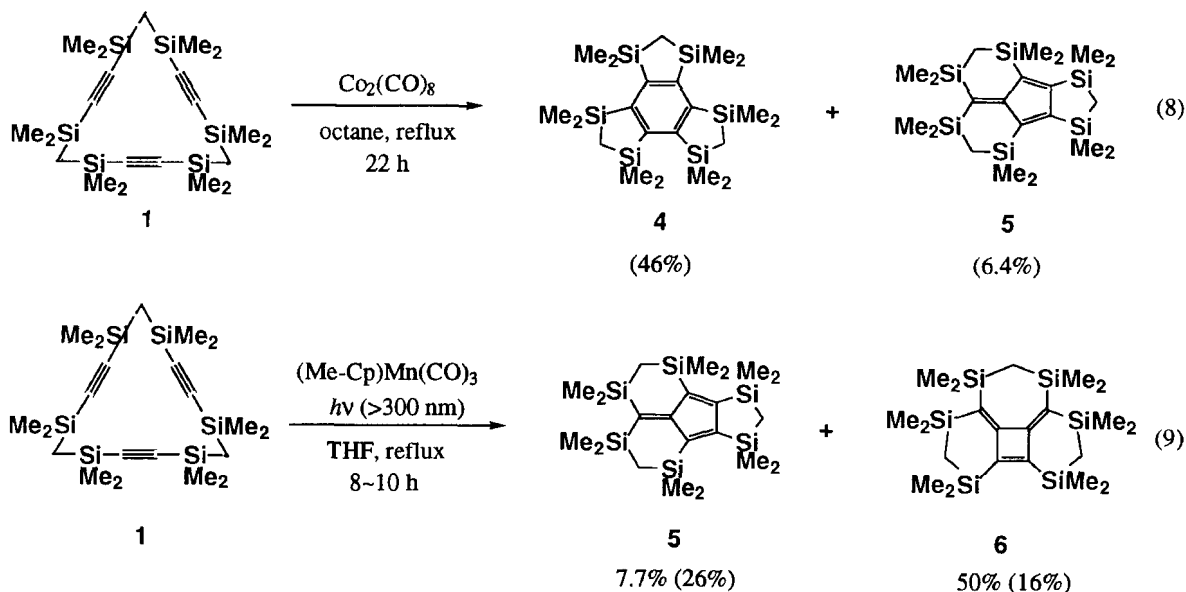
Preparation of disilmethylene-bridged cyclic polyacetylenes

Preparation of the disilmethylene-bridged cyclic polyacetylenes is rather straightforward by the coupling reactions of the respective dichlorosilanes with bis(ethynyl) Grignard reagents in fair to good yields as shown below.



Intramolecular trimerization

First, intramolecular trimerization of the cyclic triacetylene **1** was examined. The reaction catalyzed by dicobaltoctacarbonyl gave mainly a benzene derivative (**4**) but the reaction in the presence of 1.0 equiv. of (Me-Cp)Mn(CO)₃ with irradiation afforded fulvene (**5**) and dimethylenecyclobutene (**6**) derivatives.



This is the first example of the formation of dimethylenecyclobutene by trimerization of acetylenes. Compounds **5** and **6**, obtained as red and pale yellow crystals, respectively, are very stable and fully characterized by NMR. Interestingly in the latter reaction, the yield of dimethylenecyclobutene **6** increased by increasing temperature and *vice versa* for fulvene **5**. (Yields in parenthesis are at room temperature). Apparently, the second 1,2-silyl shift requires higher activation energy. Triple 1,2-silyl shift should give a [3]-radialene but at this moment, we are unable to observe the formation for the cyclic triacetylene system.

The molecular structure of **6** was determined by the X-ray crystallographic method. ORTEP drawings of **6** are shown in Fig. 1. As the structure of 3,4-dimethylenecyclobutene, only one example of highly distorted 1,2-di-*t*-butyl-3,4-diisopropylidene-1-cyclobutene has been reported so far. Although the latter is highly folded due to the steric compression, as seen in the side view, the cyclobutene ring is almost planar. Since the ring is held rigid by disilmethylene chains, two-electron reduction of **6** is expected to give a stable dianion that will be described later.

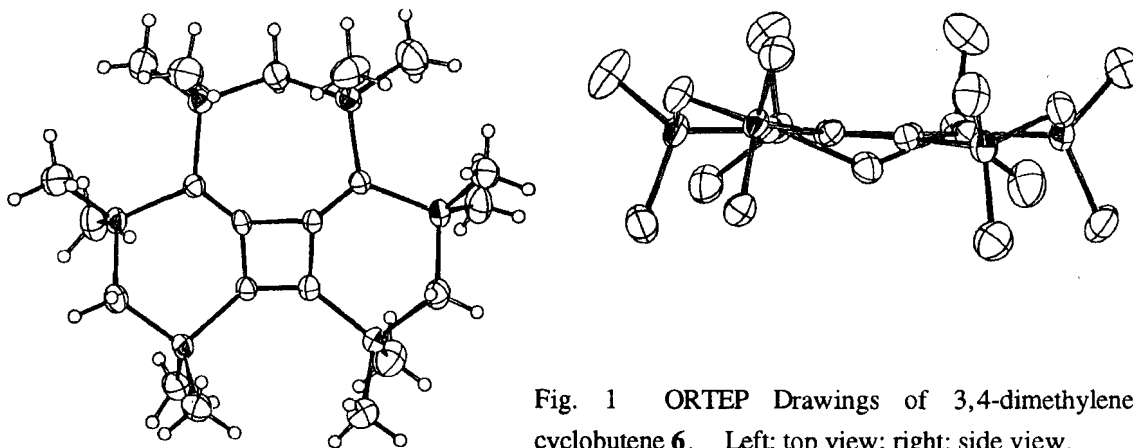
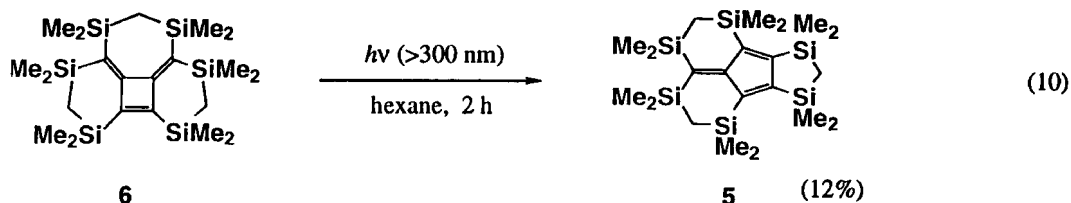
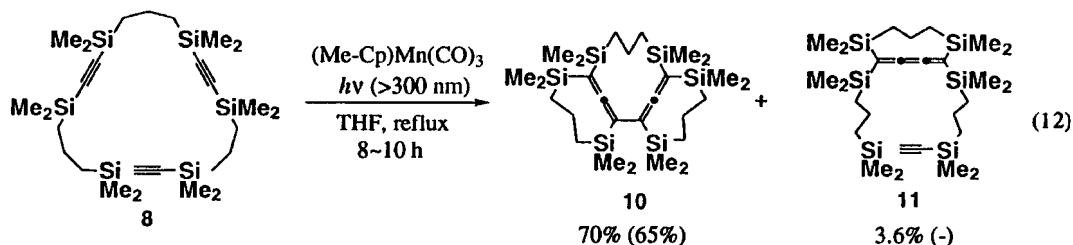
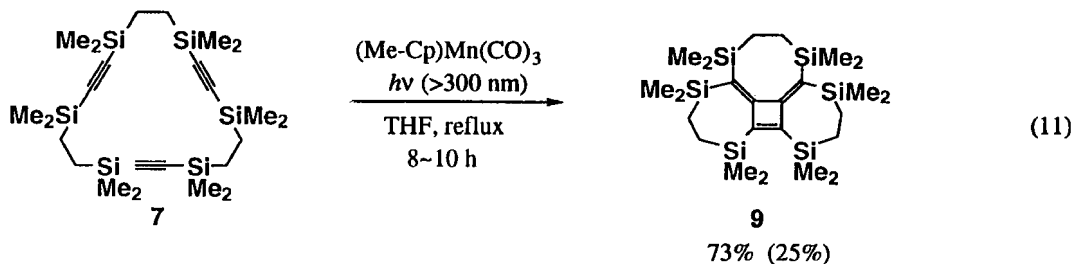


Fig. 1 ORTEP Drawings of 3,4-dimethylenecyclobutene **6**. Left: top view; right: side view.

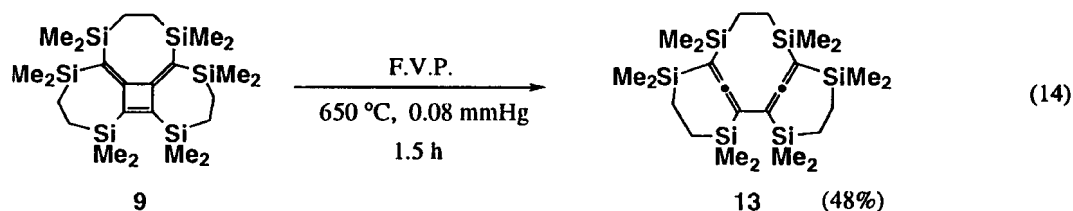
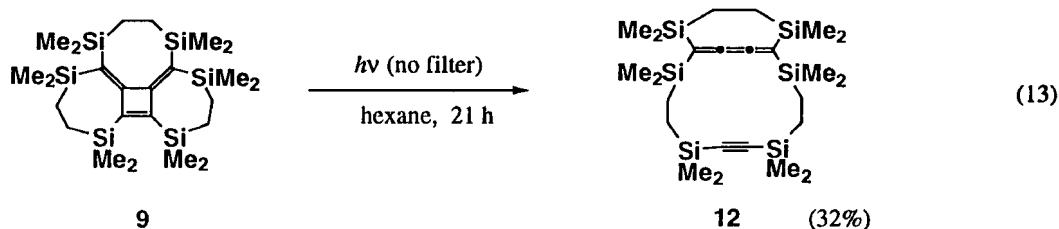
Irradiation of a hexane solution of **6** with a super high-pressure mercury arc lamp without a filter resulted in the formation of **5**. Although photochemical yield is low, the reaction which should involve reverse 1,2-silyl shift and ring enlargement is a quite unique class of isomerization.



Cyclic triacetylenes with larger tethers, i.e. disilylene- (**7**) and disilpropylene-bridged (**8**) compounds, are prepared and subjected to the Mn-complex catalyzed reaction. The compound **7** gave a dimethylenecyclobutene (**9**) similarly. At higher temperature, **9** was obtained preferably in high yield. Yields in parenthesis also indicate those at room temperature. However, the compound **8** did not give dimethylenecyclobutene any more. Instead, a biallene compound (**10**) and a small amount of butatriene (**11**) 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.

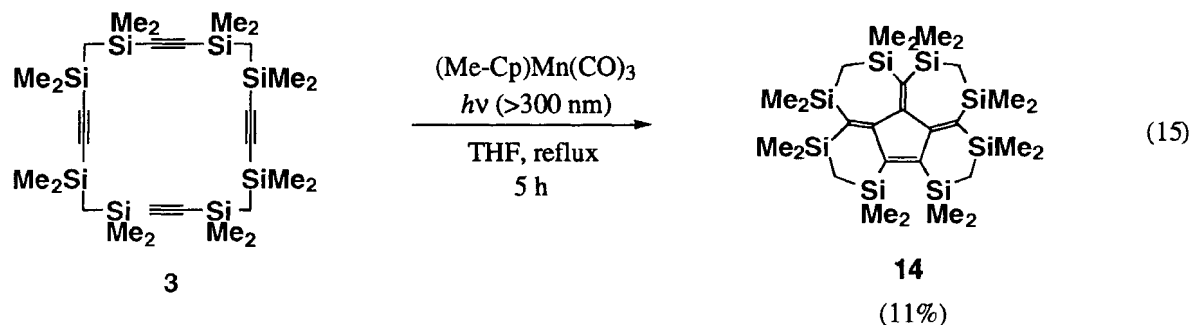


Dimethylenecyclobutene **9** also undergoes similar ring rupture upon irradiation to give **12** and by thermolysis to **13**. Difference in the mode of isomerization by photolysis and thermolysis is interesting but the reason is not clear at this moment.

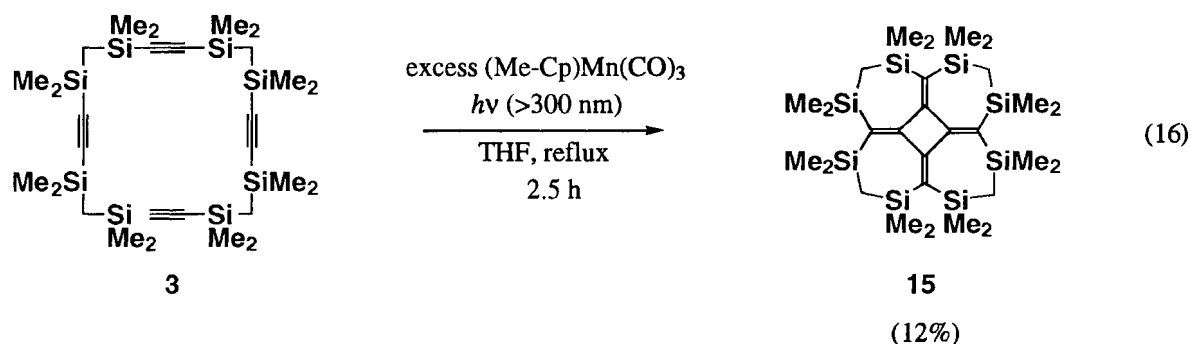


Intramolecular tetramerization

Products of cyclotetramerization of the cyclic tetraacetylene **3** would be intriguing due to the possible formation of a variety of isomers such as cyclooctatetraene, heptafulvalene, paraquinodimethane, orthoquinodimethane, trimethylenecyclopentene, and [4]-radialene. In fact, irradiation of a THF solution of **3** in the presence of an equimolar amount of (methylcyclopentadienyl)tricarbonylmanganese under reflux gave a trimethylenecyclopentene (**14**).



Interestingly, a similar reaction but with an excess (methylcyclopentadienyl)tricarbonylmanganese afforded a [4]-radialene (**15**). Triple and quadruple 1,2-silyl shift took place in these reactions, respectively. Of course, these are the first examples of cyclotetramerization of acetylenes to trimethylenecyclopentene and [4]radialene.



The structure of radialene **15** was determined by X-ray diffraction as shown in Fig. 2. As shown in the side view, **15** is not planar but distorted considerably. The dihedral angle of the 4-membered ring was 32.5° .

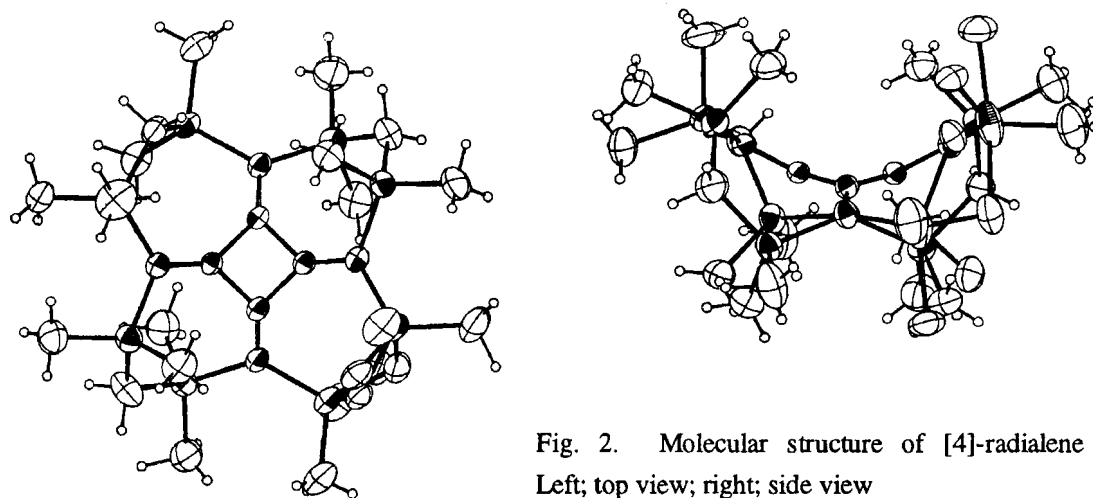
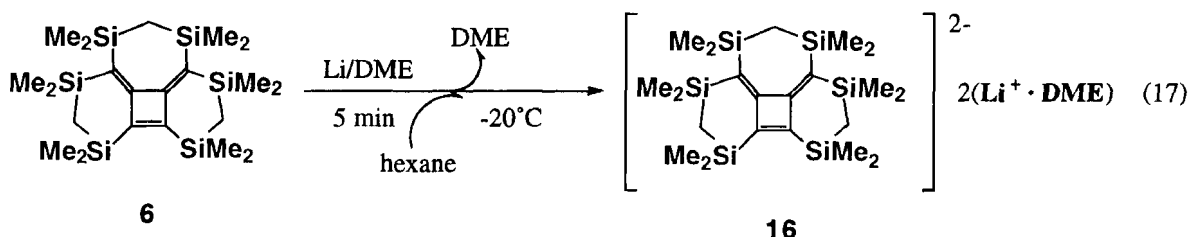


Fig. 2. Molecular structure of [4]-radialene **15**. Left; top view; right; side view

Reduction to dianions

Persilyl-substituted π electron systems can be readily reduced with lithium to dianions. Tetrakis(trimethylsilyl)ethylene (7) and silylbenzenes (8) form dianions whose structures have been determined recently. The benzene **4** can be reduced to give a stable dianion. The resulted dianion shows stable triplet ESR spectra due to planar symmetrical 8 π -electron system (9).

Reduction of the dimethylenecyclobutene **6** with lithium metal in DME produced a solution of the corresponding dianion (**16**) within 5 min. The dianion **16** was isolated as air-sensitive green crystals which were recrystallized from hexane at -20°C .



The structure of **16** was unequivocally determined by X-ray diffraction. Fig. 3 shows both top and side views of the molecular structure of **16**. Two lithiums are located up and below the plane and one DME molecule is coordinated to each lithium atom.

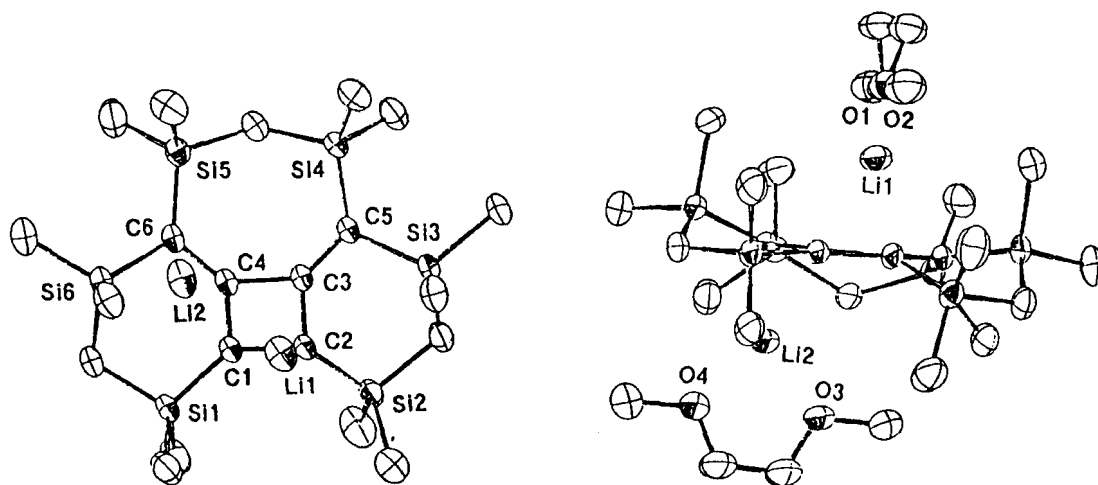
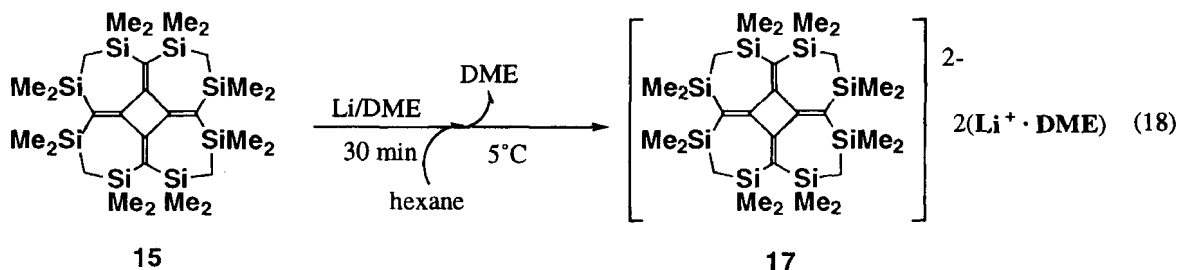


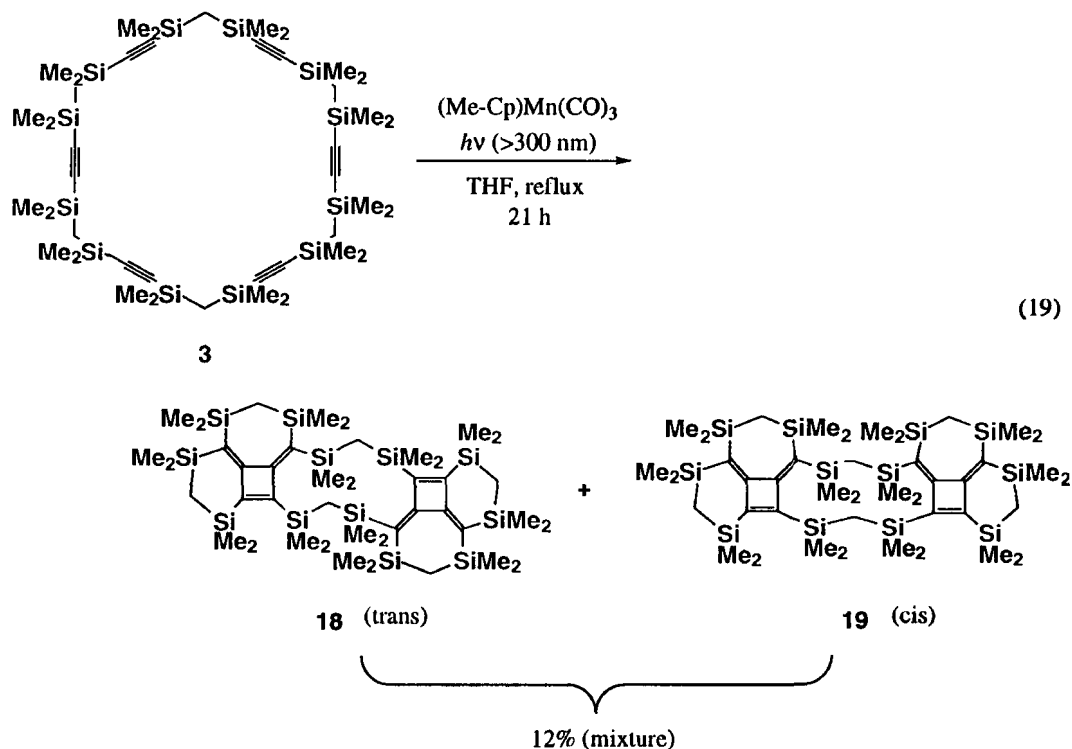
Fig. 3. ORTEP drawings of **16**. Left: top view; right: side view.

The persilylated [4]-radialene **15** was also reduced by lithium metal in DME to give a solution of the dianion. The dianion was isolated as a air-sensitive lithium complex. The structural determination is in progress.



Finally, the reaction of the macrocyclic polyacetylene **3** with (methylcyclopentadienyl)tricarbonyl-manganese under similar reaction conditions gave a isomeric mixture of bis(dimethylenecyclobutene) type products.

Transition metal complex-mediated polycyclization is thus very effective to construct a variety of novel π -electron systems. Silicon substituents play a crucial role in these reaction and modify physical properties of the products. Particularly, the formation of polyanions by reduction with alkaline metals is interesting. Further results will be reported in forthcoming publications.



Acknowledgment

The author gratefully acknowledges the effort of a gifted group in Tohoku University, where the studies are carried out (Dr. Keisuke Ebata, Dr. Chizuko Kabuto, Dr. Akira Sekiguchi, Tsukasa Matsuo, T. Inoue, and Yuko Ohtsuka). He also thanks the Ministry of Education, Science and Culture for the financial support (Specially Promoted Research No. 02102004).

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