Ring-closing Metathesis for the Synthesis of Phenylene-bridged Silamacrocycles

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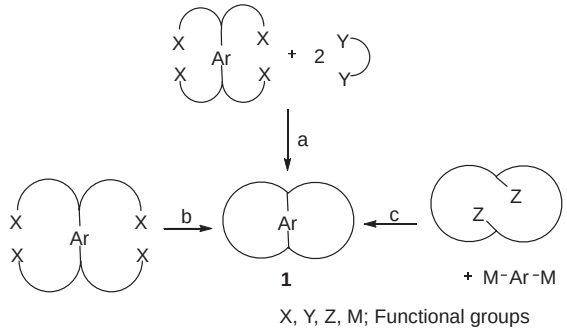
Disilacycloalkadienes with bridged halophenylene rings have been successfully synthesized via ring-closing metathesis reactions. Molecular structures of these macrocycles were fully characterized by NMR spectroscopies and X-ray crystallography. The Sonogashira coupling reactions of the macrocycles with phenylacetylene did not proceed probably owing to severe steric hindrance during the reactions.

Macrocyclic compounds with bridged π-electronic systems are of particular interest, because they are expected to have unique functions of molecular rotors as a class of molecular machines.[1] However, very few such macrocyclic systems have been synthesized so far.[2] Several strategies for the synthesis of the ring systems **1** are envisaged as shown in Scheme 1.



Scheme 1.

Method **a** requires the reactions at four sites to make two rings and hence the yield is expected to be low. Actually, phenylene-bridged polysilaalkane macrocycles **2a** and **2b** (Chart 1) were synthesized using method **a** but in very low yields (<4%).[2] Method **b** is a double cyclization and has often been effective to construct the ring systems. A molecular turnstile **3**[3] was synthesized using method **b**. To the best of our knowledge, method **c** has never been utilized for the synthesis of the ring system.[4]

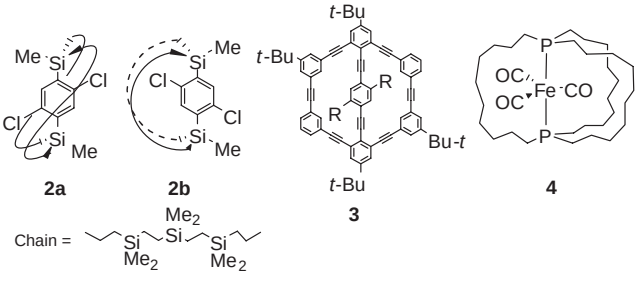
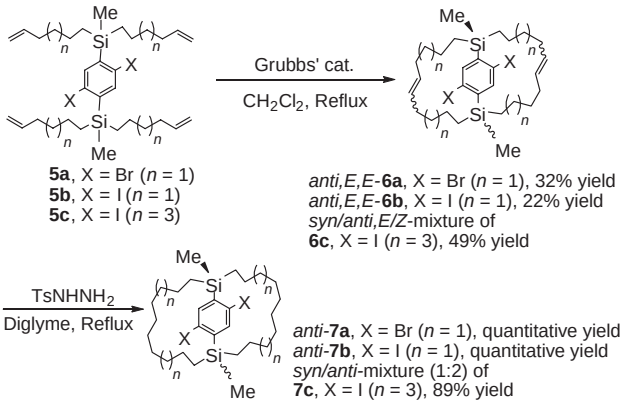


Chart 1.

Recent success of the synthesis of **4** and related bicyclic



Scheme 2.

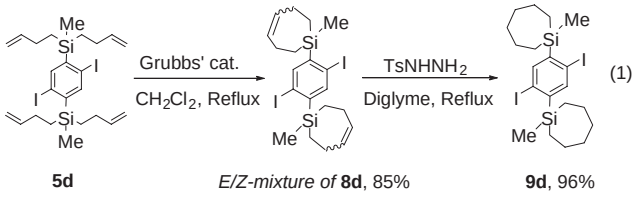
compounds[5] using the ring-closing metathesis (RCM)[6] for method **b** has encouraged us to utilize RCM for the synthesis of phenylene-bridged disilacycloalkanes **6a** and **6b**.

The RCM of 1,4-bis[di-ω-hexenyl(methyl)silyl]benzene derivatives **5a** and **5b** in the presence of a Grubbs' catalyst in dichloromethane afforded the corresponding phenylene-bridged macrocycles **6a** and **6b** as colorless solids in 32 and 22% isolated yields, respectively (Scheme 2).[7]

Among six possible geometrical isomers of **6a** (or **6b**), only anti,E,E isomer was isolated by silica-gel chromatography using toluene eluent, and then repeated washing with hexane, though reverse-phase HPLC and GPC analysis of the mixture showed the existence of other isomers and oligomeric products as minor components; syn/anti and E/Z designates the geometrical relationships of two methyl groups on silicon and two alkene junctions, respectively.[8] The hydrogenative reduction of *anti*,*E*,*E*-**6a** and *anti*,*E*,*E*-**6b** using tosylhydrazine[10] afforded the corresponding saturated macrocycles, *anti*-**7a** and *anti*-**7b**, quantitatively. Interestingly, anti,E,E selectivity is very high for the RCM of **5a** and **5b**, although syn/anti and E/Z selectivity for interligand RCM is not controlled in general.

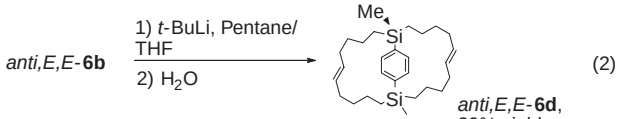
The yields and stereochemistry of phenylene-bridged silamacrocycles obtained by the RCM depend significantly on the chain-length of alkenyl substituents. The RCM of **5c** having longer alkenyl substituents gave an inseparable syn/anti and E/Z mixture of **6c** in 49%; the hydrogenative reduction of the mixture afforded **7c** with the syn/anti ratio of 1/2 in 89% yield (Scheme 2).[10] A similar RCM of 1,4-bis[di-ω-butenyl(methyl)-silyl]benzene did not produce the corresponding phenylene-bridged macrocycles; instead, a mixture of intraligand RCM products, 1,4-bis(1-methyl-1-silacycloheptenyl)benzenes **8d**, was obtained in 85% isolated yield (eq 1). The hydrogenation of **8d** gave the corresponding saturated macrocycle **9d** in 96% yield.[9] Alkenyl chain-length effects on the yields of interligand products for the RCM of bis[dialkenyl(phenyl)phosphine]platinum compounds[5a] have been shown to be similar to those

for the present RCM, while the syn/anti selectivity is different between the two RCMs.

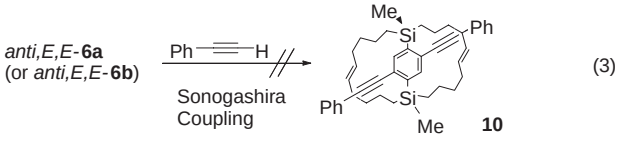


(1)

It is an interesting issue whether halogen substituents in the highly congested environment of **6a** and **6b** are replaced by other substituents. The iodine substituents of *anti*,*E*,*E*-**6b** were easily removed by *tert*-butyllithium to give the corresponding dehalogenated macrocycle *anti*,*E*,*E*-**6d** after hydrolysis (eq 2), while the debromination reaction of *anti*,*E*,*E*-**6a** with *t*-BuLi was incomplete.[9] The Sonogashira coupling reactions[11] of *anti*,*E*,*E*-**6a** and *anti*,*E*,*E*-**6b** with phenylacetylene did not proceed (eq 3),[12] suggesting severe steric hindrance during the reactions.



(2)



(3)

Molecular structures of anti,E,E isomers of **6a**, **6b**, and **6d**, *syn*,*E*,*E*-**6b**, *anti*-**7c**, and **9d** were determined by X-ray crystallography.[9,13] The X-ray structure of **6a** is shown in Figure 1. The phenylene planes of anti,E,E isomers of **6a**, **6b**, and **6d** are roughly perpendicular to the averaged plane of disilacycloalkadiene ring probably to minimize the steric contact between the macro-ring and the phenylene rings. The most stable phenylene ring conformation seems to be kept also in solution, because the alkene proton chemical shifts for anti,E,E isomers of **6a**, **6b**, and **6d** (4.74–4.90 ppm) are relatively lower than those of simple alkenes [5.5 ppm for (*E*)-2-butene].[14]

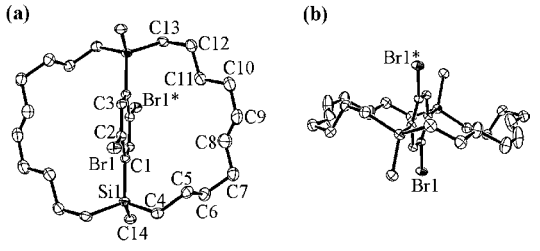


Figure 1. ORTEP drawings of *anti*,*E*,*E*-**6a** determined by X-ray crystallography. (a) side view; (b) top view. Selected bond lengths (Å) and dihedral angles (°): C8–C9 1.335(16), Si1–C1 1.900(2), C2–Br1 1.913(2), C7–C8–C9–C10 178.1(5); C14–Si1–C1–C2 179.5(2).

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan [Grant-in-Aid for Scientific Research on Specially Promoted Research (No. 17002005)].

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4 The 1,10-bridging of a 1,10-dibromo-1,4,7,10,13,16-hexasilacyclooctadecane with the di-Grignard reagent derived from 1,12-dibromododecane but the reaction gave desired compounds only in 1.5% yield: E. Kwon, K. Sakamoto, C. Kabuto, M. Kira, *Silicon Chem.* **2002**, *1*, 391.
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7 A mixture of **5a** (0.628 g, 0.96 mmol), Grubbs' catalyst, 1st generation (0.04 g, 5 mol %), and dichloromethane (200 mL) was refluxed at 50 °C for 7 h. Removal of solvent in vacuo, silica-gel column chromatography using toluene eluent, and then repeated washing with hexane afforded *anti*,*E*,*E*-**6a** (0.20 g, 32% yield) as colorless crystals. Similar reactions of **5b** afforded *anti*,*E*,*E*-**6b** in 23% yield. *anti*,*E*,*E*-**6a**: mp: 260–261 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 0.36 (s, 6H, $SiCH_3$), 0.55–1.77 (m, 32H, CH_2), 4.88 (t, 4H, CH=, $J = 3.6$ Hz), 7.48 (s. 2H, PhH); ^{13}C NMR (100 MHz, $CDCl_3$) δ − 3.78, 12.78, 23.96, 31.22, 32.38, 129.87, 130.05, 140.31, 144.30; ^{29}Si NMR (79 MHz, $CDCl_3$) δ 4.48 (SiMe); Anal. Calcd for $C_{28}H_{44}Br_2Si_2$ (MW: 596.63): C, 56.37; H, 7.43%. Found: C, 56.33; H, 7.53%. *anti*,*E*,*E*-**6b**: mp: 278–279 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 0.37 (s, 6H, $SiCH_3$), 0.51–1.80 (m, 32H, CH_2), 4.90 (t, 4H, CH=, $J = 3.6$ Hz), 7.73 (s, 2H, PhH); ^{13}C NMR (100 MHz, $CDCl_3$) δ − 3.27, 12.22, 24.08, 31.19, 32.49, 105.87, 129.87, 147.86, 148.52; ^{29}Si NMR (79 MHz, $CDCl_3$) δ 5.61 (SiMe). Anal. Calcd for $C_{28}H_{44}I_2Si_2$ (MW: 690.63): C, 48.69; H, 6.42%. Found: C, 48.76; H, 6.50%.
8 Very small amounts of syn-E,E isomers of **6a** and **6b** (0.5% for each) were isolated through recycled HPLC among the mixture.[9]
9 See Supporting Information available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
10 For hydrogenation of sila-macrocycles using tosylhydrazine, see: E. Kwon, K. Sakamoto, C. Kabuto, M. Kira, *Chem. Lett.* **2000**, 1416. For full characterization of **7a**–**7c**, see Supporting Information.[9]
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12 The Sonogashira coupling reactions of *anti*,*E*,*E*-**6a**, *anti*,*E*,*E*-**6b**, and *anti*-**7a** and *anti*-**7b** using $Pd[PPh_3]_4$, $Pd[PPh_3]_2Cl_2$, $Pd[P(t\text{-}Bu)_3]_2Cl_2$, or $PdCl_2$ were unsuccessful. No reaction occurred between *anti*,*E*,*E*-**6a** (or *anti*,*E*,*E*-**6b**) and cuprous phenyl acetylide. However, the Sonogashira coupling reactions of **5a** and **5b** with trimethylsilylacetylene took place smoothly to afford expected coupling products in up to 80% isolated yields.[9] These results will be published in a forthcoming paper, together with the data for the RCM of the coupling product.
13 Crystal data for *anti*,*E*,*E*-**6a**: $C_{28}H_{44}Br_2Si_2$, *M*r: 596.63, colorless prism, $0.20 \times 0.20 \times 0.10$ mm^3, monoclinic, space group $P2_1/c$, $a = 9.084(1)$, $b = 16.127(1)$, $c = 9.967(1)$ Å, $\beta = 101.627(2)°$, $V = 1430.3(2)$ Å^3, $Z = 2$, $D_{calc} = 1.385$ g cm^{-3}, Mo Kα ($\lambda = 0.7107$ Å), $T = 223$ K, 3277 unique reflections were collected, 2593 observed [$I > 2\sigma(I)$]. Final *Goof* = 1.04, $R1 = 0.0358$ [$I > 2\sigma(I)$], 164 parameter. Crystallographic data of anti,E,E isomers of **6a**, **6b**, and **6d**, *syn*,*E*,*E*-**6b**, *anti*-**7c**, and **9d** have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-646084, CCDC-646083, CCDC-646082, CCDC-654124, CCDC-654125, and CCDC-65426, respectively.[9]
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Published on the web (Advance View) August 29, 2007; doi:10.1246/cl.2007.1180