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

Son Thanh Phan, Wataru Setaka,\* and Mitsuo Kira\*

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578

(Received June 13, 2007; CL-070640; E-mail: setaka@mail.tains.tohoku.ac.jp; mkira@mail.tains.tohoku.ac.jp)

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  $\pi$ -electronic systems are of particular interest, because they are expected to have unique functions of molecular rotors as a class of molecular machines.<sup>1</sup> However, very few such macrocyclic systems have been synthesized so far.<sup>2</sup> Several strategies for the synthesis of the ring systems **1** are envisaged as shown in 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%).<sup>2</sup> Method **b** is a double cyclization and has often been effective to construct the ring systems. A molecular turnstile **3**<sup>3</sup> was synthesized using method **b**. To the best of our knowledge, method **c** has never been utilized for the synthesis of the ring system.<sup>4</sup>



Recent success of the synthesis of 4 and related bicyclic



compounds<sup>5</sup> 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- $\omega$ -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).<sup>7</sup>

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.<sup>8</sup> The hydrogenative reduction of *anti,E,E*-**6a** and *anti,E,E*-**6b** using tosylhydrazine<sup>10</sup> 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).<sup>10</sup> A similar RCM of 1,4-bis[di- $\omega$ -butenyl(methyl)silyl]benzene did not produce the corresponding phenylenebridged 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.<sup>9</sup> Alkenyl chain-length effects on the yields of interligand products for the RCM of bis[dialkenyl(phenyl)phosphine]platinum compounds<sup>5a</sup> have been shown to be similar to those for the present RCM, while the syn/anti selectivity is different between the two RCMs.



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.<sup>9</sup> The Sonogashira coupling reactions<sup>11</sup> of *anti*,*E*,*E*-**6a** and *anti*,*E*,*E*-**6b** with phenylacetylene did not proceed (eq 3),<sup>12</sup> suggesting severe steric hindrance during the reactions.



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.<sup>9,13</sup> 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].<sup>14</sup>



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).

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- 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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 0.36 (s, 6H, SiCH<sub>3</sub>), 0.55-1.77 (m, 32H, CH<sub>2</sub>), 4.88 (t, 4H, CH=, J = 3.6 Hz), 7.48 (s. 2H, PhH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 3.78, 12.78, 23.96, 31.22, 32.38, 129.87, 130.05, 140.31,$ 144.30; <sup>29</sup>Si NMR (79 MHz, CDCl<sub>3</sub>)  $\delta$  4.48 (SiMe); Anal. Calcd for C<sub>28</sub>H<sub>44</sub>Br<sub>2</sub>Si<sub>2</sub> (MW: 596.63): C, 56.37; H, 7.43%. Found: C, 56.33; H, 7.53%. anti,E,E-6b: mp: 278-279°C; <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 0.37 (s, 6H, SiCH<sub>3</sub>), 0.51-1.80 (m, 32H, CH<sub>2</sub>), 4.90 (t, 4H, CH=, J = 3.6 Hz), 7.73 (s, 2H, PhH);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  – 3.27, 12.22, 24.08, 31.19, 32.49, 105.87, 129.87, 147.86, 148.52;  $^{29}$ Si NMR (79 MHz, CDCl<sub>3</sub>)  $\delta$ 5.61 (SiMe). Anal. Calcd for C<sub>28</sub>H<sub>44</sub>I<sub>2</sub>Si<sub>2</sub> (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.<sup>9</sup>
- 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.<sup>9</sup>
- 11 For a recent review of Sonogashira coupling reactions, see: R. Chinchilla, C. Najera, Chem. Rev. 2007, 107, 874.
- 12 The Sonogashira coupling reactions of *anti,E,E-6a*, *anti,E,E-6b*, and *anti-7a* and *anti-7b* using Pd[PPh<sub>3</sub>]<sub>4</sub>, Pd[PPh<sub>3</sub>]<sub>2</sub>Cl<sub>2</sub>, Pd[P(t-Bu)<sub>3</sub>]<sub>2</sub>Cl<sub>2</sub>, or PdCl<sub>2</sub> 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.<sup>9</sup> 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<sub>28</sub>H<sub>44</sub>Br<sub>2</sub>Si<sub>2</sub>, *M*r: 596.63, colorless prism, 0.20 × 0.20 × 0.10 mm<sup>3</sup>, monoclinic, space group  $P2_1/c$ , a = 9.084(1), b = 16.127(1), c = 9.967(1) Å,  $\beta = 101.627(2)^\circ$ , V = 1430.3(2) Å<sup>3</sup>, Z = 2,  $D_{calc} = 1.385 \text{ g cm}^{-3}$ , Mo K $\alpha$  ( $\lambda = 0.7107$  Å), T = 223 K, 3277 unique reflections were collected, 2593 observed  $[I > 2\sigma(I)]$ . Final *Goof* = 1.04, *R*1 = 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.<sup>9</sup>
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