320 *Organometallics* **2008,** *27,* 320–323

Synthesis, Structure, and Facile Ring Flipping of a Bicyclo[1.1.0]tetrasilane

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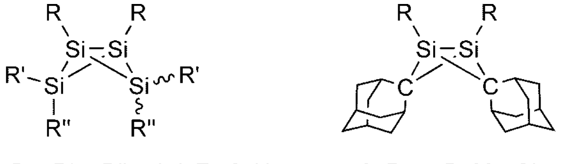
Received November 13, 2007

*Summary: Hexakis(tert-butyldimethylsilyl)bicyclo[1.1.0]tetrasilane (**3**), which is known to isomerize to the corresponding cyclotetrasilene **4** above 0 °C, was synthesized via an alternative synthetic route and isolated at low temperatures as air-sensitive yellow crystals. The short-bond structure of **3** was disclosed by X-ray analysis and DFT calculations, and facile ring flipping of **3** below 0 °C with the activation parameters of* $\Delta H^{\ddagger} = 6.67 \pm 0.18$ *kcal* mol^{-1} *and* $\Delta S^{\ddagger} = -22.7 \pm 0.8$ *cal* mol^{-1} K^{-1} *was observed.*

Silabicyclo[1.1.0]butanes ($Si_nC_{4-n}R_6$ (n = 1–4)) are unique, highly strained cyclic silicon compounds because they possess structural and electronic properties that are not observed in all-carbon bicyclo[1.1.0]butanes.[1,2] One of the most interesting structural features of the silabicyclo[1.1.0]butanes is the existence of bond stretch isomers.[3,4] Theoretically, the parent silabicyclo[1.1.0]butanes are predicted to have two isomers that are primarily different in the bonding nature of the bridge bond: short-bond and long-bond isomers.[5] The short-bond (SB) isomer has a normal bent σ-bond, while the long-bond (LB) isomer has an inverted σ-bond that results from the overlap between the back lobes of the hybridized orbitals on the bridgehead atoms. Theoretical calculations have shown that while the parent bicyclo[1.1.0]tetrasilane[5a–d,f,h] and 1,3-disilabicyclo[1.1.0]butane[5f] prefer the LB structure, the relative stabilities of the SB and LB forms are sensitive to the electronic and steric effects of the substituents at the bridgehead positions.[5h,i] Gordon et al. has shown that the replacement of the bridgehead hydrogens in the parent bicyclo[1.1.0]tetrasilane by *tert*-butyl groups results in a 2–5 kcal mol^{-1} energy preference for the short-bond isomer at the GVB/3-21G* level.[5h] Bulky aryl-substituted bicyclo[1.1.0]tetrasilanes have been reported to exist only as SB isomers using B3LYP and MP3 calculations.[5i]

Chart 1



1a, R = *t*-Bu, R' = R'' = 2,6-$Et_2C_6H_3$
1b, R = *t*-Bu_3Si, R' = H, R'' = *t*-Bu_3Si

2, R = *t*-$BuMe_2Si$

Very few experimental studies have been reported on the structure of silabicyclobutanes.[6–11] Masamune et al. reported the synthesis of the first stable bicyclo[1.1.0]tetrasilane **1a** (Chart 1), which is assignable to an SB isomer, in 1985.[6] Wiberg et al. reported the synthesis of the isomeric bicyclo[1.1.0]tetrasilanes *endo*,*endo*- and *endo*,*exo*-**1b**, but without a detailed analysis of their molecular structures.[7] We have synthesized the 1,3-disilabicyclo[1.1.0]butane **2**, which has been characterized as the first stable LB isomer by X-ray, NMR, and theoretical analyses.[8] Stable 2,4-disilabicyclo[1.1.0]butane and 1,2,3-trisilabicyclo[1.1.0]butane have been also reported by Fritz[9] and Sekiguchi,[10] respectively.

In a previous paper, we reported that hexakis(*tert*-butyldimethylsilyl)bicyclo[1.1.0]tetrasilane (**3**) was formed by the photochemical reactions of the cyclotetrasilene **4**[12a,b] and cyclotrisilene **5**[12c] (Scheme 1). The bicyclotetrasilane **3** has not been isolated, however, because of its facile isomerization to cyclotetrasilene **4** at ambient temperature via a 1,2-silyl migration pathway.

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(1) For reviews on bicyclo[1.1.0]butanes, see: (a) Wiberg, K. B. *Adv. Alicycl. Chem.* **1968**, *2*, 185. (b) Hoz, S. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z. Ed.; Wiley: New York, 1987; p 1121. (c) Hall, H. K., Jr.; Padia, A. B. *J. Polym. Sci., Part A* **2003**, *41*, 625.

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(3) For reviews on bond stretch isomerism, see: (a) Parkin, G. *Chem. Rev.* **1993**, *93*, 887. (b) Grützmacher, H.; Breher, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 4006. (c) Breher, F. *Coord. Chem. Rev.* **2007**, *251*, 1007.

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(8) Iwamoto, T.; Yin, D.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2001**, *123*, 12730.

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10.1021/om7011375 CCC: $40.75

Scheme 1. Photochemical Formation of the Hexasilylbicyclo[1.1.0]tetrasilane 3

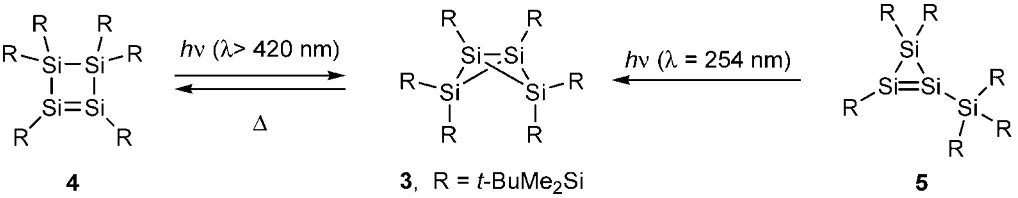
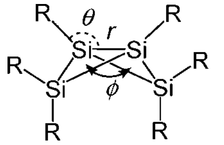


Table 1. Selected Structural Parameters of the Bicyclo[1.1.0]tetrasilane 3 and Related Compounds

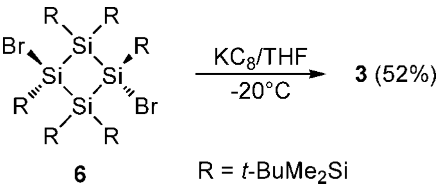


compd	r/Å	φ/deg	θ/deg	Σ(Si)[a]/deg	$\delta_{\mathrm{Si(B)}}$[b]	$\delta_{\mathrm{Si(BH)}}$[c]
3	2.367(1)	129.25(4)	149.14(4)	359.16(4)	−90.6	−145.1
			150.95(4)	359.59(4)		
1a[d]	2.373(3)	121.0	146.26	358.64	−12.0[e]	−81.0[e]
			147.48	359.00		
7-SB (calcd)[f]	2.380	120.0	146.1			
7-LB (calcd)[g]	2.859	142.2	92.20	309.28	43.5	−244.6
8-LB (calcd)[g]	2.678	138.0	107.79	333.92	13.9	−212.9
				333.91	13.7	−213.2
9-SB (calcd)[g]	2.397	120.6	137.78	358.53	−108.3	−168.2
			137.79	358.99	−102.3	−168.3

[a] The sum of the bond angles around the bridgehead silicon atom, except for those concerning the bridge bond. [b] Chemical shifts of the bridge silicon nuclei relative to tetramethylsilane. [c] Chemical shifts of the bridgehead silicon nuclei relative to tetramethylsilane. [d] Reference 6. [e] Reference 24. [f] Calculated at the GVB/3-21G* level.[5h] [g] The optimized structure was calculated at the B3LYP/6-31G(d) level. No **7**-SB, **8**-SB, and **9**-LB were located as local minima at this level. GIAO calculations were carried out at the B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) level.

In this paper, we achieved the isolation of **3** at low temperature via an alternative synthetic route and characterized its unique structural features in the solid state and in solution. The cyclotetrasilane **3** was found to adopt the short-bond structure due to the steric effects of bulky *t*-BuMe$_2$Si groups at the bridgehead silicon atoms. Although **3** isomerized to the cyclotetrasilene **4**, **3** showed facile ring flipping at temperatures lower than −30 °C. The rates and activation parameters for the ring flipping were determined by dynamic NMR analysis.

Bicyclotetrasilane **3** was synthesized by the Wurtz-type coupling reaction of 1,3-dibromocyclotetrasilane **6** with potassium graphite (2.0 equiv) at −20 °C (eq 1).[13] Keeping the resulting dark red suspension below −30 °C, filtration, and recrystallization from hexane at −30 °C gave pure **3** as yellow crystals in 52% yield.[15] When the reduction of **6** was carried out over 0 °C, cyclotetrasilene **4** was mainly obtained, probably via the thermal isomerization of the initially formed **3**.



(1)

Recrystallization from hexane at −30 °C gave single crystals of **3** suitable for X-ray crystallographic analysis. The molecular structure and selected structural parameters of **3** determined by the X-ray analysis are shown in Figure 1 and Table 1, respectively.[16] The four-membered ring of **3** is folded with an interflap angle (φ) between two three-membered-ring planes of 129.25(4)° (Table 1). The bridge Si1−Si2 bond distance (r) is 2.367(1) Å, which is slightly shorter than that of Masamune's bicyclotetrasilane **1a** (2.373(3) Å).[6] The Si2−Si1−Si5 and Si1−Si2−Si10 angles (θ) are slightly wider (149.14(4), 150.95(4)°) than those of **1a**. Since the structural parameters r, φ, and θ of **3** are close to those of **1a**, which was assigned to be a short-bond isomer, bicyclotetrasilane **3** may also be assigned as a short-bond (SB) isomer. The bridgehead silicon atoms Si1 and Si2 adopt almost planar geometries, with the sums of the bond angles around Si1 and Si2, except for those concerning the central bridge bond, being 359.16(4) and 359.59(4) °, respectively (Figure 1b); the central bridge Si−Si bond is made by overlap between almost pure 3p orbitals of bridgehead silicon atoms.[17]

To elucidate the structural characteristics of **3** more in detail, DFT calculations at the B3LYP/6-31G(d) level were performed for model bicyclotetrasilanes **7**–**9** (Chart 2). The structural parameters of their optimized geometries are given in Table 1.

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(12) (a) Kira, M.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1996**, *118*, 10303. (b) Iwamoto, T.; Kira, M. *Chem. Lett.* **1998**, 227. (c) Iwamoto, T.; Tamura, M.; Kabuto, C.; Kira, M. *Organometallics* **2003**, *22*, 2342.

(13) The prerequisite dibromocyclotetrasilane **6** is prepared by treatment of hexakis(*tert*-butyldimethylsilyl)cyclotrisilane (**10**)[14] with lithium followed by 1,2-dibromoethane. Details of the preparation of **3** and **6** are shown in the Supporting Information.

(14) Kira, M.; Iwamoto, T.; Maruyama, T.; Kuzuguchi, T.; Yin, D.; Kabuto, C.; Sakurai, H. *Dalton Trans.* **2002**, 1539.

(15) **3**: air-sensitive yellow crystals; mp <0 °C dec; ^{1}H NMR (400 MHz, toluene-d_8, 243 K, δ) 0.44 (s, 12H, Si−Me), 0.46 (s, 24H, Si−Me), 1.20 (s, 54H, *t*-Bu); ^{1}H NMR (400 MHz, toluene-d_8, 208 K, δ) 0.44 (s, 12H, Si−Me), 0.48 (s, 12H, Si−Me), 0.50 (s, 12H, Si−Me), 1.23 (s, 54H, *t*-Bu); ^{13}C NMR (100 MHz, THF-d_8, 208 K, δ) −0.9, 3.4 (br), 17.9 (br), 19.8 (br), 20.5, 27.6, 28.8, 30.1; ^{29}Si NMR (79.5 MHz, toluene-d_8, 208 K, δ) −145.1 (*Si*(SiMe$_2$-*t*-Bu)), −90.6 (*Si*(SiMe$_2$-*t*-Bu)$_2$), 3.7 (br, Si(*Si*Me$_2$-*t*-Bu)$_2$), 8.1 (br, Si(*Si*Me$_2$-*t*-Bu)$_2$), 8.7 (Si(*Si*Me$_2$-*t*-Bu)); UV-vis (3-methylpentane, 230 K) $\lambda_{\max}$/nm ($\epsilon/10^3$) 299 (16.6), 390 (2.6), 459 (1.3). Anal. Calcd for $C_{36}H_{90}Si_{10}$: C, 53.78; H, 11.28. Found: C, 53.68; H, 11.19. The UV−vis spectra of **3** are remarkably temperature dependent between 110 and 230 K, with an isosbestic point at 395 nm (see Figure S1 in the Supporting Information).

(16) Crystal data of **3** (−150 °C): $Si_{10}C_{36}H_{90}$, FW = 803.96, monoclinic, $P2_1/c$, a = 12.114(3) Å, b = 33.003(7) Å, c = 13.766(3) Å, β = 111.041(1)°, V = 5136(2) Å^3, Z = 4, D_{calcd} = 1.040 g/cm^3, R1 = 7.2%, wR2 = 13.5%, GOF = 1.32.

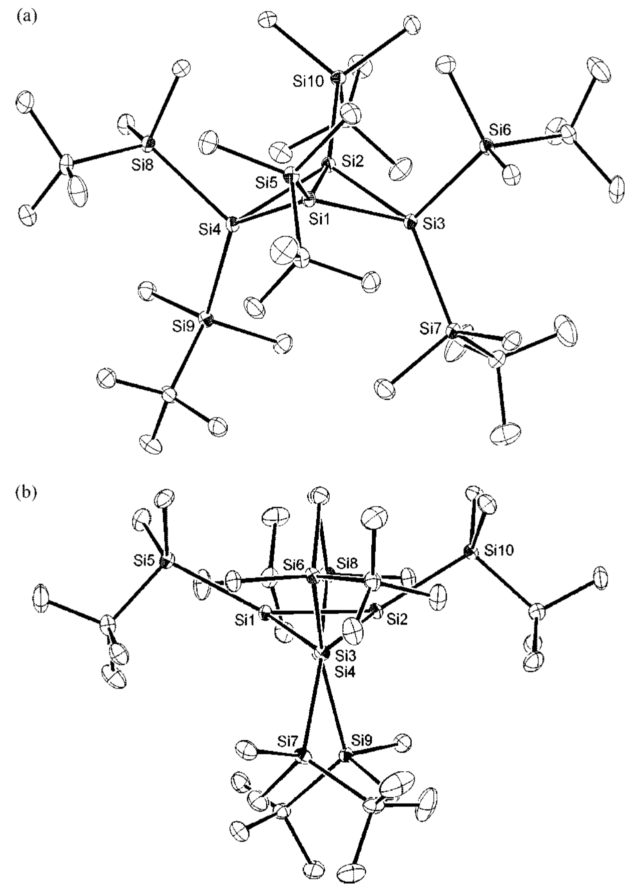
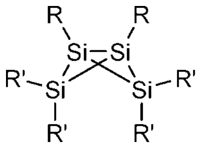


Figure 1. Two different views of the molecular structure of the bicyclo[1.1.0]tetrasilane **3**. Thermal ellipsoids are drawn at the 30% probability level.

Chart 2



7, R = R' = H
8, R = R' = SiH_3
9, R = $SiMe_3$, R' = SiH_3

In accordance with previous theoretical studies,[5] the parent bicyclotetrasilane **7** and hexasilylbicyclotetrasilane **8** optimized at the B3LYP/6-31G(d) level are characterized as long-bond isomers with long r, large φ, and small θ, while no energy minima for the short-bond isomers of **7** and **8** were located.[19] In good accord with the study of Gordon et al.,[5h] the optimized structures of bicyclotetrasilanes are very sensitive to the steric effects on the bridgehead substituents. The optimized geometry of bicyclotetrasilane **9**, where bridgehead silyl groups in **8** are replaced by bulkier trimethylsilyl groups, is completely different from those of **7** and **8**. Bicyclotetrasilanes **7** and **8** are assigned to LB isomers, while **9** is an SB isomer. The sets of structural parameters observed for **1a** and **3** are largely different from those for the optimized geometries of **7** and **8** but similar to those for **9**. The present theoretical studies allow us to assign **3** as an SB isomer and to ascribe the origin as the steric effects between the two bulky *t*-$BuMe_2Si$ substituents at bridgehead silicon atoms. The ^{29}Si resonances for the ring silicon nuclei of **3** appearing at −145.1 (bridgehead silicons) and −90.6 (bridge silicons) at 208 K are in good accord with those of **9** evaluated by GIAO calculations (Table 1), suggesting that **3** adopts the SB structure also in solution.

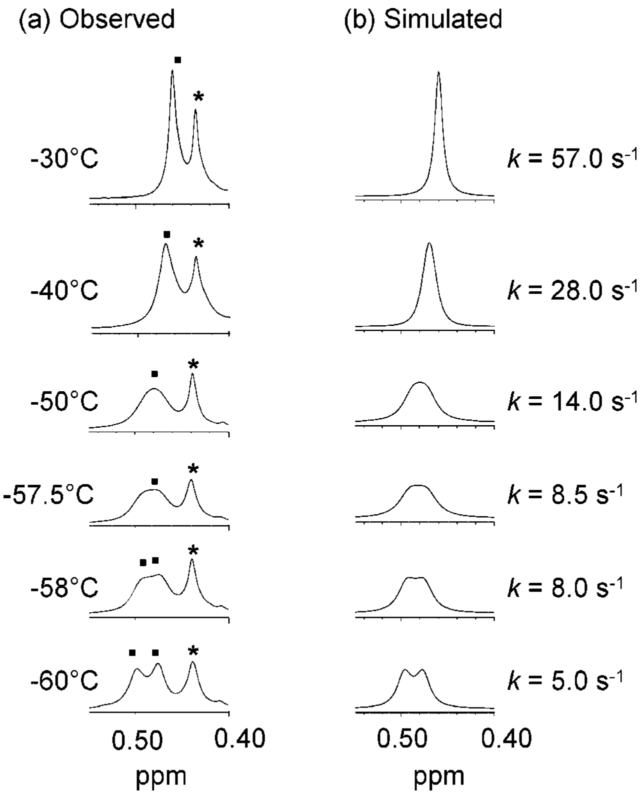


Figure 2. Observed (left, in toluene-d_8; dots denote R^b and asterisks $R^{b'}$) and calculated (right) line shapes of ^1H NMR signals due to methyl protons on silicon atoms of **3** at various temperatures. The rate constants k shown are those used for the spectral simulation.

Although the bicyclotetrasilane **3** adopts a folded structure in the solid state, ^1H NMR of **3** at 243 K in toluene-d_8 shows that the four bridge *t*-$BuMe_2Si$ groups are equivalent magnetically, suggesting facile ring flipping in solution (eq 2). To disclose the dynamic behavior of **3**, ^1H NMR spectra of **3** were recorded at various temperatures (Figure 2, left). Two peaks due to Si-CH_3 protons of the bridge *t*-$BuMe_2Si$ groups (R^b and $R^{b'}$) observed at −60 °C coalesced at −57.5 °C, and a sharp single peak was observed at −30 °C.

The temperature-dependent ^1H NMR spectra are well reproduced by a line-shape analysis using the two-site model; the spectra and flipping rate constants determined by the analysis are shown in Figure 2 (right).[20] The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values of the flipping are estimated using the Eyring plot to be 6.67 ± 0.18 kcal mol^{-1} and −22.7 ± 0.8 cal mol^{-1} K^{-1}, respectively.[21] The $\Delta H^{\ddagger}$ value for the ring flipping of **3** is much smaller than that for its isomerization to cyclotetrasilene **4** via 1,2-silyl migration ($\Delta H^{\ddagger}$ = 16.5 kcal mol^{-1}, $\Delta S^{\ddagger}$= −20.8 cal mol^{-1} K^{-1}),[12a,b] and hence,

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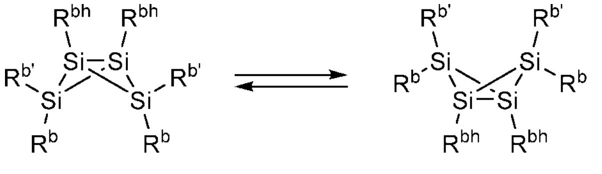
(17) The high p character of the orbitals responsible for the bridge bond has been pointed out for bicyclo[1.1.0]butanes[18] and SB isomers of bicyclo[1.1.0]tetrasilanes.[5]

(18) (a) Pomerantz, M.; Abrahamson, E. W. *J. Am. Chem. Soc.* **1966**, *88*, 3970. (b) Schulman, J. M.; Fisanick, G. J. *J. Am. Chem. Soc.* **1970**, *92*, 6653. (c) Inagaki, S.; Kakefu, T.; Yamamoto, T.; Wasada, H. *J. Phys. Chem.* **1996**, *100*, 9615.

(19) Although in previous several theoretical papers[5a–h] both LB and SB structures have been located as local minima for **7**, recent calculations for **7** at higher theoretical levels show no energy minimum at the SB structure.[5h,i]

(20) Simulation of the partial ^1H NMR spectra of **3** was performed using the gNMR program package: Peter, H. M.; *gNMR V4.1.0*; Cherwell Scientific: Oxford, U.K., 1999.

(21) For the Eyring plot, see the Supporting Information.



3 **3'**

(2)

the two processes, ring flipping and isomerization were observed independently. Using the activation parameters determined for **3**, the $\Delta G^\ddagger$ of the ring flipping is estimated to be 14.3 kcal mol^{-1} at 333 K, which is even lower than the lower limit of the $\Delta G^\ddagger$ of 15 kcal·mol^{-1}estimated at 333 K for bicyclotetrasilane **1a**.[6a] The observed $\Delta H^\ddagger$ value for **3** is quite small, compared with the barrier for ring flipping of **7** through a planar transition state estimated at the MP3/6-31G*//RHF/6-31G* level (18 kcal mol^{-1}).[22,23] The small $\Delta H^\ddagger$ value and remarkably large negative $\Delta S^\ddagger$ value for the ring flipping of **3** may suggest that the ring-flipping pathway of **3** differs from those predicted for model bicyclobutanes theoretically.[22,23] Further work seems to be required for the elucidation of the ring-flipping process.

Acknowledgment. This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan (Specially Promoted Research (No. 17002005), M.K. and T.I.) and by the Japan Society for Promotion of Science (Grant-in-Aid for Young Scientists (No. 18750025), T.I.).

Supporting Information Available: Text, figures, and tables giving details of the preparation procedures and NMR spectra of **3** and **6**, UV–vis spectra of **3**, X-ray analysis of **6**, Eyring plot of the ring flipping of **3**, and theoretical calculations for model bicyclotetrasilanes and CIF files giving X-ray crystallographic data for **3** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Collins, S.; Durler, R.; Rauk, A. *J. Am. Chem. Soc.* **1987**, *109*, 2564; **1987**, *109*, 6217. (correction). While Collins et al. have estimated the energy difference between the short-bond structure and planar transition state as the ring-flipping barrier, Gordon et al. have found a ring-flipping pathway connecting short-bond and long-bond isomers of 1,3-disubstituted bicyclotetrasilanes (1,3-$R_2H_4Si_4$ (R = H, Me, *t*-Bu)). The energy difference between the short-bond isomer and the transition state of the ring flipping is dependent on the level of theory: 7.9 kcal mol^{-1} at the GVB/6-31G(d)//GVB/3-21G* level and 17.5 kcal mol^{-1} at the MP2/6-31G(d)//GVB/3-21G* level for the parent bicyclotetrasilane (**7**).[5h]

(23) Recently a planar bicyclotetrasilane (or cyclotetrasilane-1,3-diyl), hexa-*tert*-butylbicyclo[1.1.0]tetrasilane (**11**), has been isolated by Matsumoto, Kyushin, et al.: Kurosaki, K.; Kyushin, S.; Matsumoto, H.; Kyomen, T.; Hanaya, M. 86th Annual Meeting of the Chemical Society of Japan, Chiba, Japan, March 2006, Abstract 4F4-40. The skeletal structure of **11** is similar to that assigned as the transition state for the flipping of **7**.[22] See also for related main-group-element analogues of planar cyclobutane-1,3-diyl: Scheschkewitz, D.; Amii, H.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Science* **2002**, *295*, 1880. Schoeller, W. W.; Rozhenko, A.; Bourissou, D.; Bertrand, G. *Chem. Eur. J.* **2003**, *9*, 3611.

(24) Kabe, Y. In *Synthesis and Application of Organosilicon Polymer*; Sakurai, H. Ed.; CMC: Tokyo, 1989; p 75.