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Silicon-Bridged Metacyclophanes as Parent Compounds of Silacalix[*n*]arenes. Synthesis, Structures, and Conformational Analysis by Semiempirical MO Calculations

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This paper includes the preparation of the unsubstituted silicon-bridged metacyclophanes as parent compounds of silacalix[*n*]arenes ($n = 3, 4$). A one-pot reaction gave the two different organosilicon macrocyclics, concomitantly. The structures of the metacyclophanes were unequivocally determined by X-ray crystallography. As a result, it was shown that trisila[1.1.1]metacyclophane (trisilacalix[3]arene, **1**) and tetrasila[1.1.1.1]metacyclophane (tetrasilacalix[4]arene, **2**) adopted a saddle structure and a 1,2-alternate structure, respectively. The conformations of these silacalixarenes were also analyzed by semiempirical PM3 calculations, which indicated that the conformations of the silacalixarenes in the crystal did not represent an energy minimum. A completely C_3 symmetric cone structure of **1** and a 1,3-alternate structure of **2** were estimated as the most stable conformations, respectively. In addition, a π-complex formation between the silacalixarenes and silver cation was observed by FAB mass spectrometry. This is the first observation of π-complexation of a metal ion by a [1.1.1]-metacyclophane derivative.

Introduction

Calixarenes have received intense interest due to their ability to complex metal ions and a variety of organic molecules.[1] Although there have been a large number of reports on calixarenes with carbon-bridges, only a few studies on the replacement of the calixarene bridge parts by heteroatoms have been carried out.[2] Recently, König et al. have reported the first tetrasilacalix[4]arene derivative prepared from para-*tert*-butylmethoxybenzene and dimethyldichlorosilane,[3] but no structural data of the compound in the solid state have been given so far. Very recently, unique silacalix[*n*]phosphaarenes have been reported, and their unusual π-acceptor ligand capacity has been demonstrated.[4] However, only trisila[1.1.1]*ortho*cyclophane has been prepared by Sakurai et al.,[5] and the unsubstituted parent compounds of the silacalixarenes, i.e., silicon-bridged *meta*cyclophanes have not been known. Herein we report the first successful synthesis of trisila[1.1.1]metacyclophane (trisilacalix[3]arene, **1**), obtained concomitantly with the unsubstituted tetrasila[1.1.1.1]metacyclophane (tetrasilacalix[4]arene, **2**). In addition, the structures of these new compounds in the solid state were established by X-ray crystallography. It is noteworthy that [1.1.1]metacyclophanes usually have been difficult to prepare due to the internal ring strain, and therefore, to the best of our knowledge, only a few examples of such compounds have been reported,[6] and only the structure of trithia[1.1.1]metacyclophane has been determined by X-ray analysis.[6b]

Results and Discussion

The silacalixarenes were prepared by the condensation of 1,3-dibromobenzene and dimethyldichlorosilane with magnesium in refluxing THF as shown in Scheme 1.

Although the isolated yields of the products were low (**1**: 12%, **2**: 2%), probably due to the formation of linear oligomers, the expected silamacrocycles were easily separated by fractional recrystallization and isolated as colorless needles. Their structures were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR and mass spectrometry. Finally, their structures were unequivocally determined by X-ray crystallography. The observed molecular structures are shown in Figures 1 and 2, respectively.

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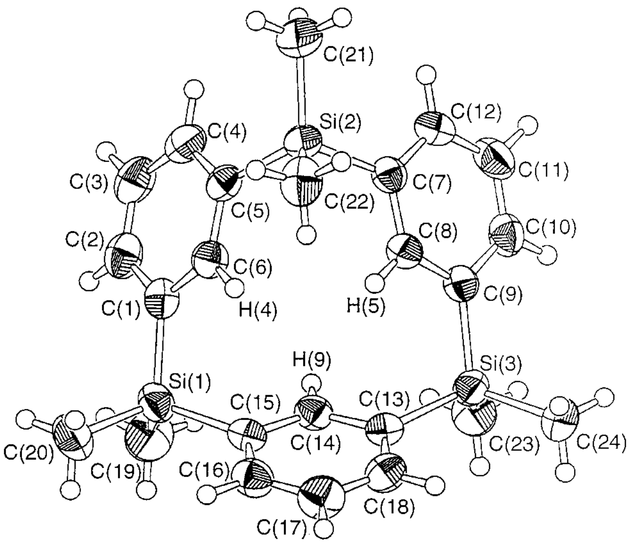


Figure 1. Molecular structure of **1** with thermal ellipsoids drawn at the 50% probability level.

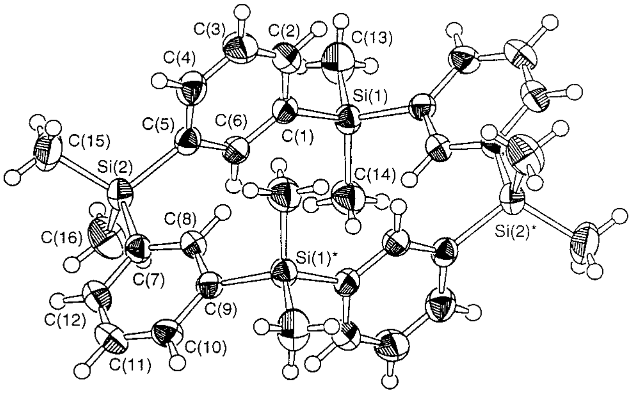
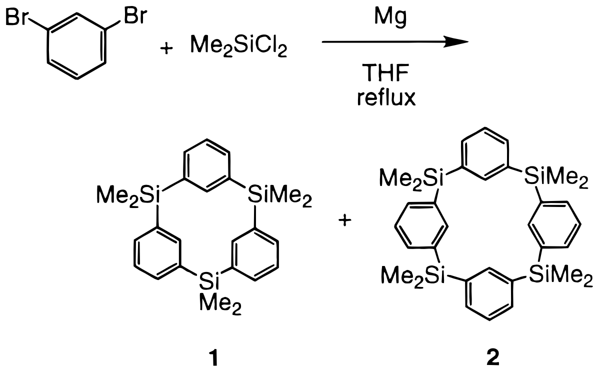


Figure 2. Molecular structure of **2** with thermal ellipsoids drawn at the 50% probability level.

Scheme 1



Important bond distances and angles are listed in Tables 1 and 2, respectively.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 1

Si(1)−C(1)	1.875(4)	Si(1)−C(15)	1.875(4)
Si(1)−C(19)	1.860(4)	Si(1)−C(20)	1.859(4)
Si(2)−C(5)	1.885(4)	Si(2)−C(7)	1.885(3)
Si(2)−C(21)	1.855(4)	Si(2)−C(22)	1.852(4)
Si(3)−C(9)	1.880(3)	Si(3)−C(13)	1.873(3)
Si(3)−C(23)	1.857(4)	Si(3)−C(24)	1.861(4)
C(1)−C(2)	1.395(5)	C(1)−C(6)	1.405(4)
C(2)−C(3)	1.370(5)	C(3)−C(4)	1.378(5)
C(4)−C(5)	1.400(5)	C(5)−C(6)	1.395(4)
C(7)−C(8)	1.393(4)	C(7)−C(12)	1.386(5)
C(8)−C(9)	1.398(4)	C(9)−C(10)	1.391(4)
C(10)−C(11)	1.379(5)	C(11)−C(12)	1.393(5)
C(13)−C(14)	1.403(4)	C(13)−C(18)	1.388(4)
C(14)−C(15)	1.396(4)	C(15)−C(16)	1.396(4)
C(16)−C(17)	1.390(5)	C(17)−C(18)	1.373(5)
H(4)···H(5)	2.524	H(5)···H(9)	2.944
H(4)···H(9)	3.117		
C(1)−Si(1)−C(15)	106.3(1)	C(1)−Si(1)−C(19)	108.6(2)
C(1)−Si(1)−C(20)	112.1(2)	C(15)−Si(1)−C(19)	109.2(2)
C(15)−Si(1)−C(20)	111.3(2)	C(19)−Si(1)−C(20)	109.2(2)
C(5)−Si(2)−C(7)	104.0(1)	C(5)−Si(2)−C(21)	112.0(2)
C(5)−Si(2)−C(22)	109.4(2)	C(7)−Si(2)−C(21)	110.7(2)
C(7)−Si(2)−C(22)	109.8(2)	C(21)−Si(2)−C(22)	110.7(2)
C(9)−Si(3)−C(13)	107.2(1)	C(9)−Si(3)−C(23)	109.0(2)
C(9)−Si(3)−C(24)	110.5(2)	C(13)−Si(3)−C(23)	109.4(2)
C(13)−Si(3)−C(24)	111.3(2)	C(23)−Si(3)−C(24)	109.5(2)
Si(1)−C(1)−C(2)	122.6(3)	Si(1)−C(1)−C(6)	121.0(3)
C(2)−C(1)−C(6)	116.1(3)	C(1)−C(2)−C(3)	121.5(4)
C(2)−C(3)−C(4)	121.0(4)	C(3)−C(4)−C(5)	120.7(3)
C(4)−C(5)−C(6)	116.7(3)	C(1)−C(6)−C(5)	123.9(3)
Si(2)−C(5)−C(4)	123.7(3)	Si(2)−C(5)−C(6)	118.8(3)
Si(2)−C(7)−C(8)	118.4(2)	Si(2)−C(7)−C(12)	124.1(3)
C(8)−C(7)−C(12)	117.0(3)	C(7)−C(8)−C(9)	124.1(3)
Si(3)−C(9)−C(8)	121.5(2)	Si(3)−C(9)−C(10)	122.1(3)
C(8)−C(9)−C(10)	116.3(3)	C(9)−C(10)−C(11)	121.3(3)
C(10)−C(11)−C(12)	120.5(3)	C(7)−C(12)−C(11)	120.6(3)
Si(3)−C(13)−C(14)	119.4(2)	Si(3)−C(13)−C(18)	124.5(3)
C(14)−C(13)−C(18)	116.0(3)	C(13)−C(14)−C(15)	124.0(3)
Si(1)−C(15)−C(14)	118.6(2)	Si(1)−C(15)−C(16)	124.8(3)
C(14)−C(15)−C(16)	116.5(3)	C(15)−C(16)−C(17)	121.2(3)
C(16)−C(17)−C(18)	119.8(3)	C(13)−C(18)−C(17)	122.4(4)

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 2

Si(1)−C(1)	1.874(2)	Si(1)*−C(9)	1.868(2)
Si(1)−C(13)	1.856(3)	Si(1)−C(14)	1.857(3)
Si(2)−C(5)	1.870(2)	Si(2)−C(7)	1.878(2)
Si(2)−C(15)	1.868(3)	Si(2)−C(16)	1.856(3)
C(1)−C(2)	1.403(4)	C(1)−C(6)	1.394(3)
C(2)−C(3)	1.378(4)	C(3)−C(4)	1.379(4)
C(4)−C(5)	1.392(4)	C(5)−C(6)	1.397(3)
C(7)−C(8)	1.388(3)	C(7)−C(12)	1.400(3)
C(8)−C(9)	1.402(3)	C(9)−C(10)	1.397(3)
C(10)−C(11)	1.380(4)	C(11)−C(12)	1.381(4)
Si(1)···Si(1)*	7.501	Si(2)···Si(2)*	8.594
C(1)−Si(1)−C(9)	107.0(1)	C(1)−Si(1)−C(13)	109.6(1)
C(1)−Si(1)−C(14)	110.9(1)	C(9)−Si(1)−C(13)	111.3(1)
C(9)−Si(1)−C(14)	108.4(1)	C(13)−Si(1)−C(14)	109.7(1)
C(5)−Si(2)−C(7)	108.4(1)	C(5)−Si(2)−C(15)	108.9(1)
C(5)−Si(2)−C(16)	111.0(1)	C(7)−Si(2)−C(15)	109.9(1)
C(7)−Si(2)−C(16)	108.9(1)	C(15)−Si(2)−C(16)	109.7(1)
Si(1)−C(1)−C(2)	118.3(2)	Si(1)−C(1)−C(6)	124.6(2)
C(2)−C(1)−C(6)	117.1(2)	C(1)−C(2)−C(3)	121.0(2)
C(2)−C(3)−C(4)	120.1(3)	C(3)−C(4)−C(5)	121.5(2)
Si(2)−C(5)−C(4)	120.3(2)	Si(2)−C(5)−C(6)	122.6(2)
C(4)−C(5)−C(6)	117.1(2)	C(1)−C(6)−C(5)	123.1(2)
Si(2)−C(7)−C(8)	121.8(2)	Si(2)−C(7)−C(12)	121.6(2)
C(8)−C(7)−C(12)	116.6(2)	C(7)−C(8)−C(9)	124.1(2)
Si(1)−C(9)−C(8)	118.6(2)	Si(1)−C(9)−C(10)	124.9(2)
C(8)−C(9)−C(10)	116.4(2)	C(9)−C(10)−C(11)	121.3(2)
C(10)−C(11)−C(12)	120.3(2)	C(7)−C(12)−C(11)	121.3(2)

For the calix[3]arene derivative, there are two possible stable conformations: a cone structure and a saddle structure in which one phenylene ring shows the upside flip from the cone structure. In our X-ray results, a saddle structure of **1** is clearly demonstrated, as in the case of trithia[1.1.1]metacyclophane.[6b] Three hydrogens on the phenylene rings lie inside of the internal 12-membered ring, and the closest interatomic distance is observed between H(4) and H(5) as ca. 2.52 Å. In connection with the distorted structure of **1** due to its relatively small internal ring size, it is noteworthy that all silicon atoms in **1** are not coplanar with the connecting phenylene rings, and especially Si(1) and Si(2) are located above the least-squares plane of the benzene ring composed of C(1)−C(6) by +0.238 and +0.307 Å, respectively. As a consequence, all Si−C_{ar} bonds bend from the phenylene plane to the extent of 6.3° (average). In addition, Si−C_{ar} bond lengths at the Si(2) position (average 1.885 Å) were slightly longer than the normal value (1.87 Å). It may be concluded that the bridging silicon atoms effectively reduce the internal 12-membered ring strain. Meanwhile, for the calix[4]arene derivative, there have been commonly suggested four conformations termed by Gutsche as the cone, partial cone, 1,2-alternate, and 1,3-alternate arrangements.[7] The other chairlike conformation in a crystalline state, however, also has been reported for an unsubstituted calix[4]arene, a methylene-bridged analogue of **2**.[8] There are the other unsubstituted calix[4]arenes, i.e., tetrathia[1.1.1.1]metacyclophane[9] and tetraaza[1.1.1.1]metacyclophane,[10] but in both cases, the 1,3-alternate conformation has been characterized by X-ray analyses. The conformation of tetrasila[1.1.1.1]metacyclophane **2** deviates somewhat from the chairlike conformation; two opposing benzene rings are nearly parallel, but no coplanar orientation of the two aromatic rings is observed. Eventually, a 1,2-alternate structure of tetrasilacalix[4]arene **2** is revealed. Interatomic distances between Si(1)···Si(1)* and Si(2)···Si(2)*, corresponding to the diameter of an internal 16-membered ring of **2**, are found to be 7.50 Å and 8.59 Å, respectively. Neither an elongation of the covalent bonds nor a significant distortion of the coordination geometry was observed in the structure of **2** indicative of its strain-free structure.

To understand the conformational isomerism in calix[*n*]arenes, computational studies on the structures of calixarenes have been investigated.[11] In our present study, semiempirical PM3 calculations[12] on the conformations of the silamacrocyclics were carried out. Calculated structures are shown in Figures 3 and 4, respectively. Relative energies of the possible conformers are shown in Table 4.

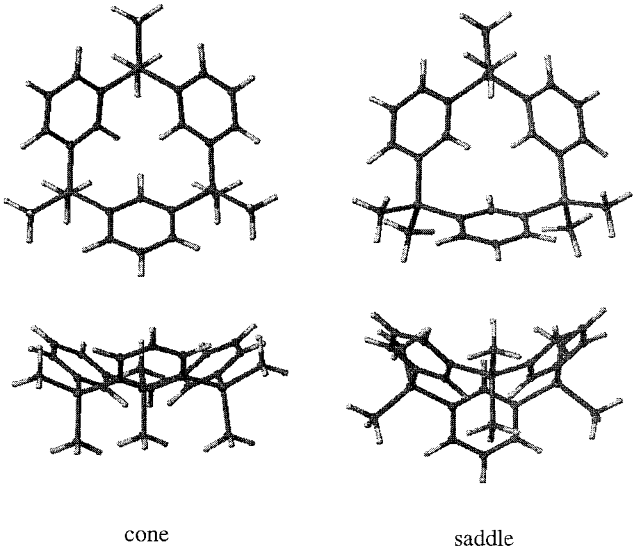


Figure 3. Possible conformers of trisila[1.1.1]metacyclophane (trisilacalix[3]arene) **1** estimated by semiempirical PM3 calculation.

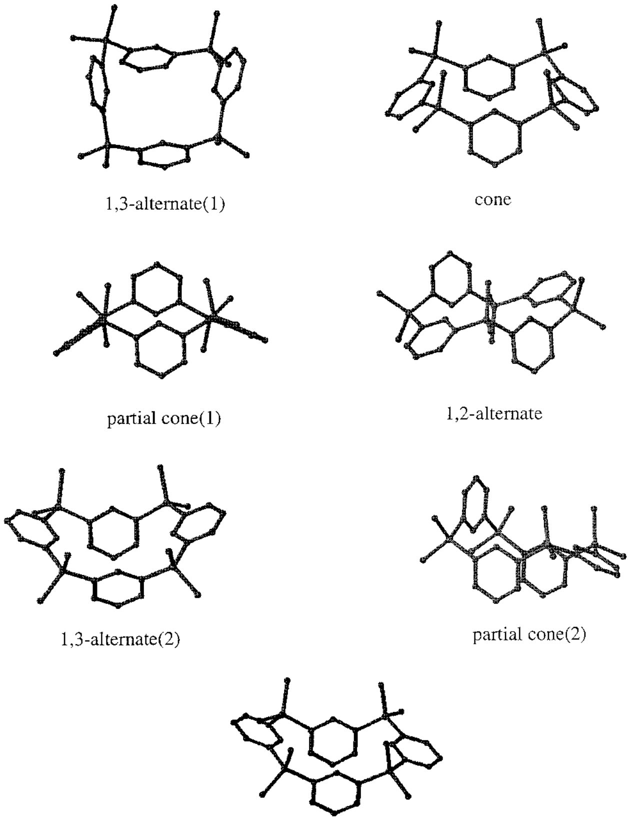


Figure 4. Possible conformers of tetrasila[1.1.1.1]metacyclophane (tetrasilacalix[4]arene) **2** estimated by semiempirical PM3 calculation (hydrogens are omitted for clarity).

Surprisingly, in the cases of both **1** and **2**, the structure determined by X-ray analysis does not lie at an energy minimum. The saddle conformation of **1** is 1.33 kcal/mol less stable than the completely C_3 symmetric cone conformation. In the case of **2**, there appears to be not four but seven possible conformers, as indicated in Figure 4; both the “1,3-alternate” and “partial cone” conformers are drawn to have isomers distinguished by phenylene geometry. However, a chairlike conformation of **2** is not observed even in this calculation. According to the calculation results, the order of stability among these seven characteristic conformations of **2** is 1,3-alternate (1) > cone > partial cone (1) > 1,2-alternate > 1,3-alternate (2) > partial cone (2) > partial cone (3). The 1,2-alternate structure of **2** observed in the solid state is found to be 0.96 kcal/mol less stable than the 1,3-alternate structure estimated to be the most stable conformer of **2**. It should be noted, therefore, that the packing of molecules in the

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Table 3. Crystal Data and Structure Refinement for 1 and 2

	1	2
formula	$C_{24}H_{30}Si_3$	$C_{32}H_{40}Si_4$
fw	402.76	537.01
temp, K	298	298
radiation	Cu Kα (λ = 1.541 78 Å)	Cu Kα (λ = 1.541 78 Å)
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
unit cell dimens	a = 6.468(1) Å, b = 20.653(2) Å, c = 17.956(3) Å, β = 90.025(8)°	a = 13.222(2) Å, b = 6.7370(6) Å, c = 18.305(2) Å, β = 95.527(6)°
vol	2398.6(5) Å^3	3315.8(7) Å^3
Z	4	2
D_{calc}	1.115 g/cm^3	1.099 g/cm^3
F(000)	864.00	576.00
μ	18.49 cm^{-1}	18.22 cm^{-1}
cryst size	0.30 × 0.10 × 0.03 mm	0.90 × 0.03 × 0.03 mm
2θ range	4−129.9°	4−129.9°
no. of data collected	4621	2869
no. of unique data	4082	2744
R, R_w	0.045, 0.052	0.045, 0.058
GOF	1.52	2.30

Table 4. Relative Energies of Conformers of 1 and 2 Estimated by Semiempirical PM3 Calculation[a]

conformation	1	2
cone	0.00	0.91
saddle	1.33	
1,2-alternate		0.96
1,3-alternate (1)		0.00
1,3-alternate (2)		1.20
partial cone (1)		0.94
partial cone (2)		1.50
partial cone (3)		1.78

[a] In kcal/mol.

crystal would induce a conformational change resulting in the reduction of the intramolecular cavity size of silacalixarenes.

Sakurai already reported that the twisted saddle conformation of ortho-bridged trisilacyclophane was determined by X-ray crystallography, and the conformer was observable even in solution by low-temperature ^{1}H NMR analyses at 203 K.[5] We also tried variable-temperature ^{1}H NMR analyses of **1** and **2** in CD_2Cl_2, but no splitting of the peaks derived from the freezing of the conformation was observed even at 188 K, not only for **2** but also for the somewhat distorted molecule **1**. Thus it is obvious that these two silacalixarenes have significant conformational flexibility in solution, as indicated in the very small differences of relative energy among the possible conformers by PM3 calculations.

To date, some of cyclophanes without any functional substituents have been known as "π-cryptands" being able to accept a silver cation.[13] In these compounds, it has been suggested that not only a specifically attractive interaction between a silver cation and π-electrons of an aromatic ring but also a rigid facing geometry of aromatic rings in the cyclophanes can provide the strong π-complexation property. However, even for the conformationally mobile calix[4]arene derivative without functional group, π-complexation with alkali metal cations has been recently detected by mass spectrometry.[14] In preliminary experiments, we have investigated a π-cryptand character of silacalixarenes and successfully observed the cation−π interaction between the silacalixarenes and a silver cation in FAB mass spectrometry experiments. As shown in Figure 5a, the mass fragment of m/z 511, as a parent peak of the π-complex, i.e., [**1** + Ag]$^+$, was clearly observed in the FAB mass spectrum of the mixture of **1** and an excess of silver triflate. In addition, isotope pattern calculation for the formula $C_{24}H_{30}Si_3Ag$ was in accord with the observed peaks at 511. A similar π-complexed fragment ion of 645, i.e., [**2** + Ag]$^+$, was also observed between **2** and the silver cation under identical conditions. These results strongly suggest the complexation of a silver cation within the trisilacalix[3]arene and tetrasilacalix[4]arene cavities. Thus the relatively high stability of the cone structure of **1** and the 1,3-alternate conformation of **2**, as estimated by PM3 calculation, are crucial for the π-complexation phenomenon in the gas phase.[15,16]

Conclusion

We have demonstrated a facile preparation of novel silacalixarenes **1** and **2** and determined their solid-state structures by X-ray crystallography. A saddle structure of **1** and a 1,2-alternate structure of **2** were found, respectively. The observed conformers **1** and **2**, however, were not consistent with the optimized structures by semiempirical PM3 calculations. Although the trisilacalix[3]phosphaarene has been recently shown to be a ligand for transition metals,[4] the present observation of cation−π interaction between unsubstituted silacalixarenes and a silver ion in FAB mass spectroscopy indicated the first evidence of the π-complexation ability for [1.1.1]-metacyclophane (calix[3]arene) derivatives. Further investigations on the π-cryptand capacity and the functionalization of the silacalixarenes are in progress.

Experimental Section

General Methods. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured on a Varian Gemini-300BB NMR spectrometer. ^{29}Si (100 MHz) NMR spectra were measured on a JEOL LA-500 NMR spectrometer. Mass spectra were measured on a Shimadzu GCMS-5050A mass spectrometer. High-mass spectra and FAB mass spectra were measured on a JEOL JMS-DX303 mass spectrometer. In the case of FAB-MS, the mixture of chloroform/m-nitrobenzyl alcohol (1:1 v/v) was used for a matrix solvent.

Preparation of Silicon-Bridged Metacyclophanes 1 and 2. Under an argon atmosphere, 1,3-dibromobenzene (25 g, 106 mmol) in dry THF (100 mL) was added slowly to a mixture of magnesium (6.18 g, 254 mmol) and dimethyldichlrosilane (13.7 g, 106 mmol) in dry THF (200 mL) at room temperature with rapid stirring. The rate of addition was adjusted to a gentle reflux. The solution was subsequently heated under reflux for 2 h and allowed to stand at room temperature for 1 h. After hydrolysis of the solution by adding

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[13] (a) Pierre, J. L.; Baret, P.; Chautemps, P.; Armand, M. *J. Am. Chem. Soc.* **1981**, *103*, 2986. (b) Kang, H. C.; Hanson, A. W.; Eaton, B.; Boekelheide, V. *J. Am. Chem. Soc.* **1985**, *107*, 1979. (c) Heirtzler, F. R.; Hopf, H.; Jones, P. G.; Bubenitschek, P.; Lehne, V. *J. Org. Chem.* **1993**, *58*, 2781. (d) Gross, J.; Harder, G.; Vögtle, F.; Stephan, H.; Gloe, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 481. (e) Seppälä, T.; Wegelius, E.; Rissanen, K. *New J. Chem.* **1998**, 789.

[14] Inokuchi, F.; Miyahara, Y.; Inazu, T.; Shinkai, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1364.

[15] Strong π-complexation behavior between some conformationally rigid 1,3-alternate calix[4]arenes and a silver cation has been reported earlier: Ikeda, A.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 3102.

[16] Similar π-complexation phenomenon of organosilicon macrocyclics is observed in the case of hexasila[2.2.2]paracyclophane as a silicon analogue of the well-known π-cryptand: Sakurai, H.; Yatabe, T.; Sekiguchi, A. To be submitted.

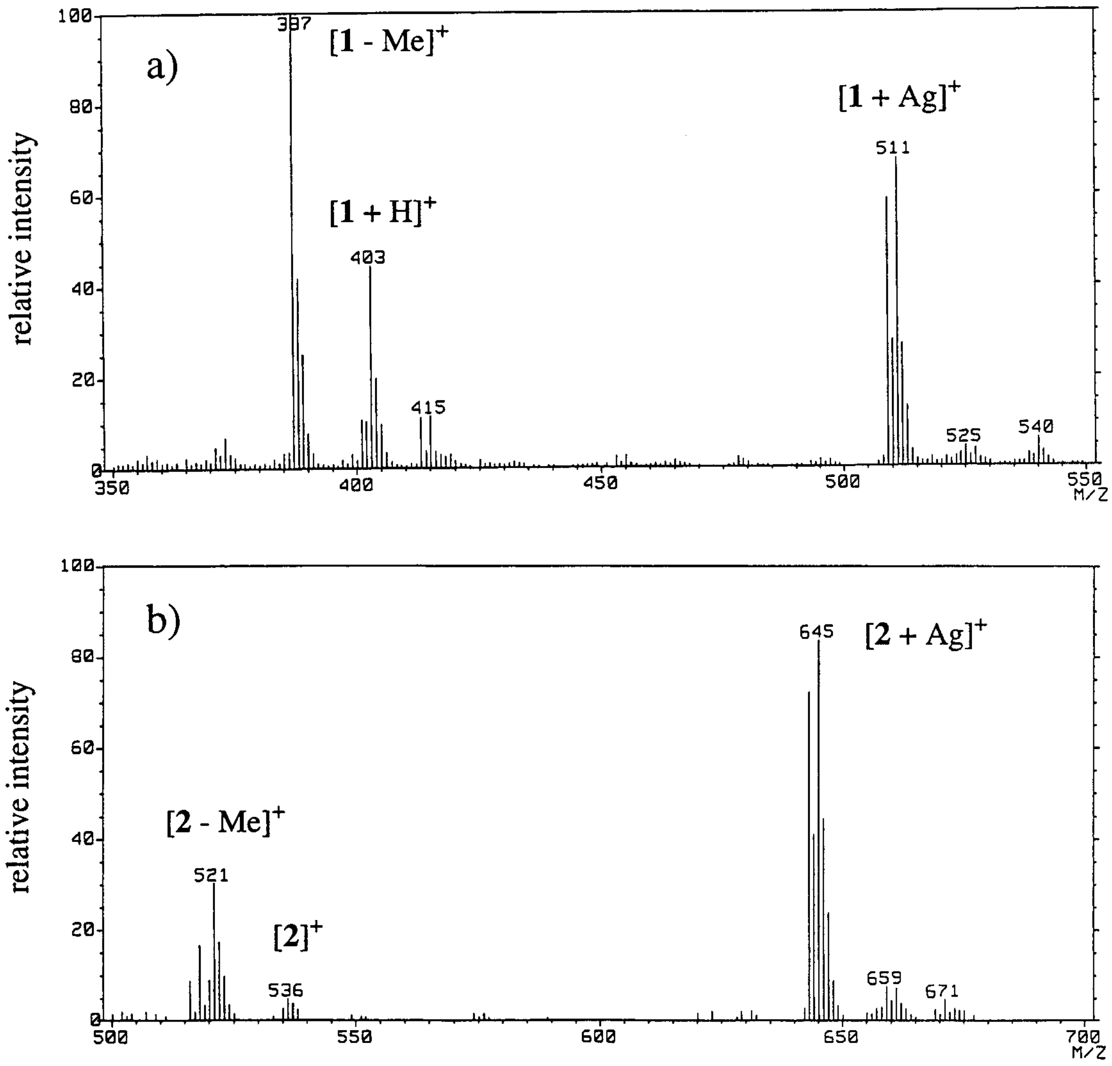

Figure 5. FAB mass spectra of the silacalixarenes with an excess amount of silver triflate in a chloroform/*m*-nitrobenzyl alcohol (1:1 v/v) mixed matrix: (1) for **1** and (2) for **2**.

water (50 mL), the organic layer was extracted by diethyl ether (100 mL) and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo, and then 320 mg (0.59 mmol) of **2** was obtained by recrystallization of the residue using the hexane/benzene (10/1) mixed solvent at 5 °C. When the filtrate was evaporated, 2.1 g of impure **1** subsequently was obtained by kugelröhr distillation of the residue (bp = 150−160 °C/0.1 mmHg) as colorless solid. After a recrystallization of the solid from an ethanol solution at room temperature, 1.70 g (4.23 mmol) of **1** was isolated. Crystals of **1** and **2** were suitable enough for X-ray crystallography without further recrystallization.

Selected data for **1**: 12% yield; colorless needles; mp 129−130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.50 (s, 18H), 7.37 (t, J = 7.5 Hz, 3H), 7.59 (d, J = 7.5 Hz, 6H), 7.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.67, 127.35, 134.42, 137.23, 142.21; ^{29}Si NMR (100 MHz, $CDCl_3$) δ −8.28; MS *m*/*z* (EI, %) 402 (M^+, 13), 387 (100), 207 (26), 186 (26); HRMS calcd for $C_{24}H_{30}Si_3$ 402.1655, obsd 402.1654.

For **2**: 2.3% yield; colorless needles; mp 228−229 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 0.40 (s, 24H), 7.25 (t, J = 7.0 Hz, 4H), 7.52 (d, J = 7.0 Hz, 8H), 7.58 (s, 4H); ^{13}C NMR (75 MHz, C_6D_6) δ −2.56, 127.53, 135.12, 137.47, 140.75; ^{29}Si NMR (100 MHz, C_6D_6) δ −7.25; MS *m*/*z* (EI, %) 536 (M^+, 23), 521 (98), 463 (32), 253 (45), 135 (62), 73 (100); HRMS calcd for $C_{32}H_{40}Si_4$ 536.2207, obsd 536.2209.

X-ray Structure Determination of 1. Data were collected on an Enraf-Nonius CAD4 diffractometer at 298 K by using graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å) and ω-scan techniques: monoclinic, space group $P2_1/n$, a = 6.468(1) Å, b = 20.653(2) Å, c = 17.956(3) Å, β = 90.025(8)°, V = 2398.6(5) Å^3, Z = 4, D_{calc} = 1.115 g/cm^3, F(000) = 864.00, μ = 18.49 cm^{-1}. Unit-cell parameters were determined by a least-squares refinement using the setting angles of 25 carefully centered reflections in the range of $37.82° < 2\theta < 56.89°$. A total of 4621 reflections were collected in the range of $4° < 2\theta < 129.9°$, of which 4082 were unique. The data were corrected for Lorentz and polarization effects. An empirical absorption correction (φ-scan) was applied (T_{max} = 0.9991, T_{min} = 0.8548). The structure was solved by direct methods (SIR92) and expanded by using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2691 observed reflections ($I > 3.00\sigma(I)$, 244 variable parameters) and converged (largest parameters was 0.008 times its esd) with unweighted and weighted agreement factors of R = 0.045, R_w = 0.052. GOF = 1.52. Crystallographic data and the results of refinements are summarized in Table 3. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC).

X-ray Structure Determination of 2. Data were collected on an Enraf-Nonius CAD4 diffractometer at 298 K by using graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å) and ω-scan techniques: Monoclinic, space group $P2_1/n$, a = 13.222(2) Å, b = 6.7370(6) Å, c = 18.305(2) Å, β = 95.527(6)°, V =

3315.8(7) Å^3, $Z = 2$, $D_{calc} = 1.099$ g/cm^3, $F(000) = 576.00$, $\mu = 18.22$ cm^{-1}. Unit-cell parameters were determined by a least-squares refinement using the setting angles of 25 carefully centered reflections in the range of 43.60° < 2θ < 60.60°. A total of 2869 reflections were collected in the range of 4° < 2θ < 129.9°, of which 2744 were unique. The data were corrected for Lorentz and polarization effects. A secondary extinction correction was also applied (coefficient: 1.81966×10^{-5}). Empirical absorption corrections (φ-scan) were applied ($T_{max} = 0.9942$, $T_{min} = 0.8678$). The structure was solved by direct methods (SIR92) and expanded by using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2314 observed reflections ($I > 1.50\sigma(I)$, 164 variable parameters) and converged (largest parameters was 0.01 times its esd) with unweighted and weighted agreement factors of $R = 0.045$, $R_w = 0.058$. GOF = 2.30. Crystallographic data and the results of refinements are summarized in Table 3. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC).

Semiempirical Calculations. Semiempirical PM3 calculations were carried out by using the CAChe MOPAC 94 programs[17] on an IBM SP2 computer.

Acknowledgment. We thank Ms. Mikiko Usui for her assistance in the mass spectrometry experiment.

Supporting Information Available: ^{1}H NMR spectra of **1** and **2** and X-ray data of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] CAChe MOPAC 94 (group server), Oxford Mol. Inc.