Synthesis, Structure, and Coordination Properties of Silicon-Bridged Macrocycles

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Received July 7, 1995[⊗]

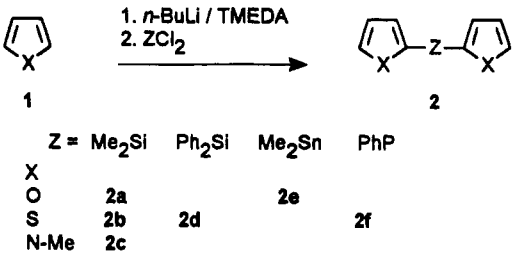
Macrocyclic compounds are obtained in one step by the reaction of carbo- and heterocyclic dianions with bis-electrophiles, such as Me_2SiCl_2, Me_2SnCl_2, or $PhPCl_2$. *p-tert*-Butylmethoxybenzene as starting material affords silacalix[4]arene **7**. The most stable conformers of **7** are determined by force field calculations. A 1,3 alternate conformation in the crystal is revealed by X-ray structure analysis for the heterocyclic silacalix[4]arenes **3a** and **3c**, while **3b** shows a partial cone conformation. The ability of the macrocycles to extract metal ions from the aqueous phase is investigated in competition experiments. The tested macrocycles extract metal ions, however, with less affinity than crown ethers.

Molecular recognition requires correspondence in the shape of the receptor and the substrate molecule, or between lock and key in the words of Emil Fischer.[1] Macrocycles can provide the necessary preorganization of the "host" for the inclusion process, and therefore most artifical receptors for ions or neutral "guests" are cyclic molecules.[2] Carbon is the common bridging element in natural and synthetic macrocycles such as porphyrins or calixarenes. However, other elements such as silicon, tin, or phosphorus might replace carbon as a link between rigid subunits to give macrocycles with new binding properties. Condensation or substitution reactions are widely used in macrocyclic syntheses.[3] The smooth reaction of organoalkali compounds with chlorosilanes, tin, or phosphorus halides is suitable for the construction of carbon-element bonds.[4] If carbo- or heterocyclic dianions and bis-electrophiles, such as Me_2SiCl_2, are employed in this reaction, macrocyclic compounds are obtained in one step.[5] The good solubility of sila-macrocycles in nonpolar organic solvents renders them suitable receptors for membrane transport of metal ions.

Results and Discussion

The facile deprotonation of thiophene, furan, and *N*-methylpyrrole in the 2- or 5-position by a strong base such as *n*-BuLi/TMEDA is a well-known process.[4] A wide variety of bis-electrophiles react with the anions to give dimers **2**[6] in high yield (Scheme 1). Extension of this reaction to dianions allows the synthesis of cyclic compounds. By treatment of the aromatic heterocycles with 2 equiv of the kinetically fast base *n*-BuLi/TMEDA/KO*t*-Bu[7] in hexane complete deprotonation at the 2- *and* 5-position is achieved. Slow addition of a solution of Me_2SiCl_2 in hexane gave the macrocyclic tetramers **3a–c**[8] and hexamers **4a,b** in yields up to 35% (Scheme 2). The

Scheme 1



[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1995.

(1) Fischer, E. *Ber. Dtsch. Chem. Ges.* **1894**, *27*, 2985–2993.

(2) Dietrich, B.; Viout, P.; Lehn, J.-M. *Macrocyclic Chemistry,* VCH: Weinheim, 1993.

(3) (a) Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests,* Monographs in Supramolecular Chemistry, Royal Society of Chemistry, 1994; (b) Diederich, F. *Cyclophanes*, Monographs in Supramolecular Chemistry, Royal Society of Chemistry, 1991; for the synthesis of macrocycles from dilithio intermediates see: (c) Lin, J.; Pang, Y.; Young, V. G.; Barton, Th. J. *J. Am. Chem. Soc.* **1993**, *115*, 3794–3795. (d) Yang, X.; Knobler, C. B.; Zheng, Z.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1994**, *116*, 7142–7159.

(4) Schlosser, M. Organoalkali Reagents in *Organometallics in Synthesis*; Wiley: New York, 1994; pp 1–166.

(5) König, B.; Rödel, M.; Bubenitschek, P.; Jones, P. G. *Angew. Chem.* **1995**, *107*, 752–754. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 661–662.

(6) Some of these dimeric compounds have been previously synthesized. **2a**: (a) Gevorgyan, V.; Borisova, L.; Lukevics, E. *J. Organomet. Chem.* **1992**, *441*, 381–387. (b) Lukevits, E.; Erchak, N. P.; Matorykina, V. F.; Mazheika, I. B. *J. Gen. Chem. USSR* **1983**, *53*, 959–967. **2b**: (c) Yi, S.; Ohashi, S.; Sato, H.; Nomori, H., *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1244–1247. (d) Furukawa, N.; Hoshiai, H.; Shibutani, T.; Higaki, M.; Iwasaki, F.; Fujihara, H. *Heterocycles* **1992**, *34*, 1085–1088. **2d**: (e) Spialter; Harris, *U.S. Atomic Energy Comm. WADC-TR-58-276*, **1959**, *1*, 4. **2e**: (f) Lukevics, E.; Erchak, N. P.; Shatts, V. D. *Khim. Elementorg. Soedin.* **1976**, 56–63. **2f**: (g) Horner, B.; Roeder, R. *Phosphorus Relat. Group V Elem.* **1976**, *6*, 147–148. Due to the restricted availability of some of these sources we have included the spectroscopic data of compounds **2c–f** into the supporting information.

(7) (a) Brandsma, L. *Preparative Polar Organometallic Chemistry 1*; Springer: Berlin, 1990. (b) Wakefield; B. J. *Organolithium Methods*; Academic Press: London, 1988; thiophene is sufficently acidic to be deprotonated in the 2,5-positions by *n*-BuLi/TMEDA in hexane.

(8) (a) Only the tetrameric structure **3b** was isolated in the previously reported reaction of a thiophene dimer with Me_2SiCl_2: Kauffmann, Th.; Kniese, H.-H. *Tetrahedron Lett.* **1973**, *14*, 4043–4046. (b) Chicart, P.; Corriu, R. J. P.; Moreau, J. E.; Garnier, F.; Yassar, A. In *Inorganic and Organometallic Polymers with Special Properties*; Laine, R. M., Ed.; NATO ASI Series, 1992; Vol. 206, pp 179–190.

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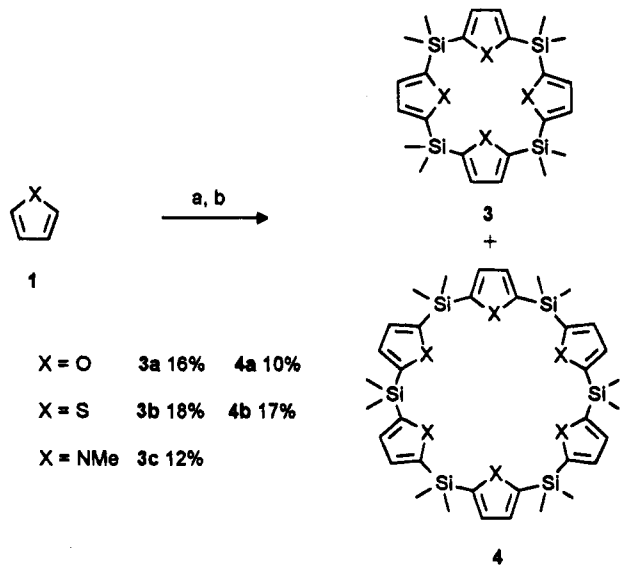
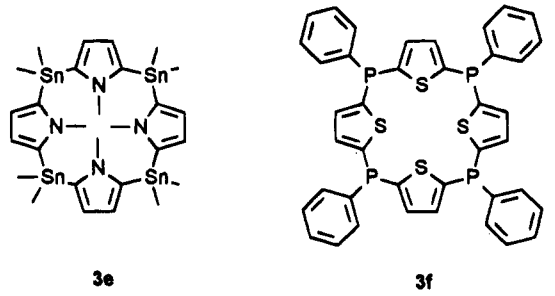
Scheme 2



Scheme 3



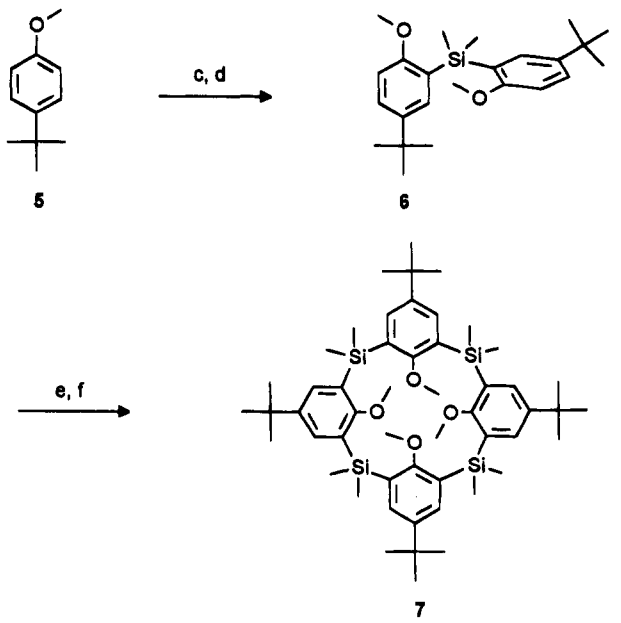
fast reaction of the organolithium compounds with Me_2SiCl_2 allows the synthesis of the cyclic structures at organoalkali concentrations of 10^{-2} M.

All macrocycles, with the exception of **4a**, are high melting, crystalline solids, readily soluble in nonpolar organic solvents. While the hexa- and tetrameric structures of thiophene and furan were obtained in nearly equal amounts, the sila-porphyrinogen **3c** was the only isolated cyclic structure from *N*-methylpyrrole. Macrocycles with other ring sizes could be detected in traces only by mass spectroscopy from the reaction mixtures.

Other elements such as phosphorus or tin can substitute for silicon in the macrocyles. Compound **3e** and **3f** (Scheme 3) were synthesized from the heterocyclic dianions and Me_2SnCl_2 or $PhPCl_2$ as described above. The nearly identical NMR spectra of **3e**[9] and **3c** indicate the similar structure of both compounds. **3e** is rather unstable and decomposes rapidly if stored in air. While all other sila-heterocalixarenes are mobile compounds in solution, two isomers of the phosphorus-bridged macrocycle **3f** were obtained. The shift of the ^{31}P resonance shows the formal oxidation level +3 for the phosphorus bridge.[10]

Methoxy groups have a strong *ortho* directing effect in the lithiation of aromatic rings.[11] However, the stabilization is insufficient to allow the formation of

Scheme 4



dianions. Therefore a stepwise procedure is necessary to obtain cyclic structures from *p-tert*-butylanisole and Me_2SiCl_2. Monolithiation of **5** and reaction with Me_2SiCl_2 gave the crystalline dimer **6**, which was characterized by X-ray structure analysis.[5] Bislithiation of **6** was achieved with 2 equiv of *n*-BuLi/TMEDA at room temperature, and subsequent slow addition of 1 equiv of Me_2SiCl_2 yielded *p-tert*-butylsilacalix[4]arene **7** in 16% isolated yield (Scheme 4). The simple proton NMR spectra of **7** indicates conformational mobility at room temperature in solution. At lower temperatures the signals broaden significantly, but defined conformers, as in the case of the carbocyclic analogue *p-tert*-butylcalix[4]arene,[12] are not observed. The longer silicon–carbon bridges in **7** facilitate the rotation of the aromatic units.

The results of the molecular mechanics calculations[13] with respect to the lowest energy conformers of **7** are summarized in Table 1. The notation of the conformers by digits and letters indicating the orientation of the anisole rings and the inward/outward direction of the methoxy groups follows the designation proposed by Fischer.[14] The order of stability among the four characteristic conformations of **7** obtained by MM3 calculations is partial cone (most stable) > 1.3-alternate > 1.2-alternate ≫ cone (least stable). Much the same prefer-

(9) Proton- and carbon-NMR spectra of **3e** show coupling to tin nuclei.

(10) The isomers could not be separated by chromatography. The geometry of the isomers could not be derived from the spectroscopic data.

(11) Crowther, G. P.; Sundberg, R. J.; Sarpeshkar, A. M. *J. Org. Chem.* **1984**, *49*, 4657–4663.

(12) (a) Groenen, L. C.; van Loon, J.-D.; Verboom, W.; Harkema, S.; Casnati, A.; Ungaro, R.; Pochini, A.; Ugozzoli, F.; Reinholdt, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 2385–2392. (b) Gutsche, C. D.; Dhawan, B.; Levine, J. A.; No, K. H.; Bauer, L. J. *Tetrahedron* **1983**, *39*, 409–426.

(13) (a) For each of the four main conformations of **7** all possible orientations of the methoxy groups were generated and the energy was subsequently minimized. The *tert*-butyl substituents of **7** were replaced by methyl groups to save computational time. All minimizations were done using the MM3(94) force field running on an IBM RISC/6000 workstation. The missing parameter for the $O-C_{aromatic}-C_{aromatic}-Si$ torsion angle was obtained by means of the MM3 parameter estimator. In the calculations the block diagonal Newton–Raphson method followed by a full-matrix optimization was used. (b) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551–8566. (c) Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8566–8575. (d) Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8576–8582. (e) For a describtion of possible calixarene conformers see: Gutsche, C. D. *Calixarenes*, Monographs in Supramolecular Chemistry, Royal Society of Chemistry: Cambridge, 1992; p 87 –126.

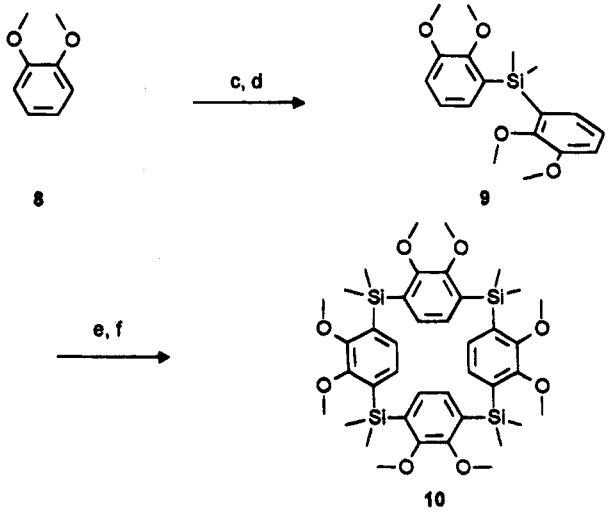
(14) Fischer, S.; Grootenhuis, P. D. J.; Groenen, L. C.; van Hoorn, W. P.; van Veggel, F. C. J. M.; Reinhouldt, D. N.; Karplus, M. *J. Am. Chem. Soc.* **1995**, *117*, 1611–1620.

Table 1. Relative Energies[a] of the Most Stable Conformers of 7

conformation	code[b]	E_{bond}	E_{vdW}	E_{elec}	ΔE_{rel}
partial cone	0001-ABAB	0.00	0.00	0.00	**0.00**
1.3-alternate	0101-BABA	−1.73	−0.39	2.45	**0.33**
1.2-alternate	0011-ABAB	1.38	−1.04	0.48	**0.82**
cone	0000-AABA	2.32	0.65	0.48	**3.45**

[a] All energies in kcal mol^{-1}; $E_{bond} = E_{compression} + E_{bend} + E_{bend\text{-}bend} + E_{stretch\text{-}bend} + E_{torsion} + E_{torsion\text{-}stretch}$; E_{vdW} denotes the sum of all van der Waals interactions; E_{elec} denotes the energy resulting from the electrostatic term, FSE denotes the final steric energy. [b] Code according to ref 14.

Scheme 5



ence for the partial cone conformation has been previously reported for the tetramethyl ether of *p-tert*-butylcalix[4]arene (85% at −30 °C in $CDCl_3$).[15] The reduced steric strain and enlarged cavity size of silacalix[4]arene due to the longer Si−C bond compared to a C−C bond allows stable conformers with one or two inward orientated methoxy groups. The stability of the conformers is determined by the balance of repulsive interactions from close contacts of Me_2Si and methoxy groups and the repulsive interactions resulting from the inward orientation of adjacent methoxy groups. A measure for the enlarged cavity size of **7** is the distance of opposite bridging silicon atoms. The corresponding values for *p-tert*-butylcalix[4]arene are given for comparison in parentheses: 8.17/8.17 (7.19/7.16) Å for partial cone, 8.21/8.24 (7.17/7.16) Å for 1.3-alternate, 7.65/8.64 (6.75/7.64) Å for 1.2-alternate, and 8.27/8.15 (7.17/7.19) Å for the cone conformation.

1,2-Dimethoxybenzene (**8**) was converted into the dimer **9** and cyclized to macrocycle **10**[16] by the same procedure (Scheme 5). Octamethoxysila[1.1.1.1]paracyclophane (**10**) is, like **7**, a mobile compound at room temperature. A separation of the NMR signals is observed at −90 °C, indicating that the rotation of the aromatic rings or the *pseudo*-rotation of the *gem*-methyl groups becomes slow on the NMR time scale.[17]

Table 2. Extraction of Metal Salts from Aqueous Solutions[a]

	benzo-15-crown-5[b]	**3b**	**4b**	**3c**	**3a**	**10**
Pb^{2+}	21	−[c]	14	–	–	–
Ni^{2+}	–	–	–	–	–	12
Na^{+}	31	7	11	16	–	–
K^{+}	15	8	8	10	–	–
Hg^{2+}	8	–	–	8	30	8
Cu^{2+}	–	–	7	12	9	10
Al^{3+}	10	–	13	9	–	–

[a] Values given are percent extracted from the aqueous phase. Aqueous phase is 10% HNO_3 and contains 22 different salts with a concentration of 50 ppm each. Other anions present are sulfate and phosphate. Cations that show a change in concentration of less than 5% after the extraction are not listed. The organic phase is dichloromethane and contains 100 ppm of the receptor molecule. Extractions were performed for 24 h by vigorous stirring at room temp. [b] For extraction experiments with benzo-15-crown-5 see ref 15b and cited refs. [c] Change in concentration of less than 5%.

Extraction experiments were used to determine the binding properties of the new macrocycles to metal ions. To facilitate this process an effective screening procedure was developed. Contrary to the described procedures for extraction coefficient determination that use a single metal salt in each run,[18] mixtures of up to 22 different metal salts in aqueous acidic solution were extracted with organic solvents containing the potential receptor. The concentration of all ions in the aqueous phase were simultaneously determined by the ICP-AES technique[19] before and after the extraction step. From these competition extraction experiments neither single extraction coefficients nor binding constants can be derived. However, the affinity and general selectivity of a macrocycle toward several metal ions are obtained in one run. The results, summarized in Table 2, show a smaller affinity of the silicon-bridged macrocycles in metal salt extractions compared to crown ethers. However, the observed selectivity of extraction is in some cases remarkably high. Thus **3a** is a particular good chelator for mercury ions.[20]

X-ray Crystallographic Analyses. The structure of **3a**[21] in the crystal shows a 1,3-alternate conformation of the macrocycle (Figure 1). The dimensions of the cavity are ca. 565 pm (Si6−Si14) × 562 pm (Si22−Si14). A very similar conformation and packing in the crystal was observed for **3c** (Figure 2). The X-ray structure analysis of **3b**,[5] which displays crystallographic inversion symmetry, shows a flattened partial cone conformation in the

(15) (a) Harada, T.; Rudzinski, J. M.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 2* **1992**, 2109−2154. (b) Harada, T.; Rudzinski, J. M.; Osawa, E.; Shinkai, S. *Tetrahedron* **1993**, *49*, 5941−5954. (c) The energy differences form force field calculations between the conformers of *p-tert*-butylcalix[4]arene are very small. Fischer et al. have corrected the obtained potential energies for the conformational degeneracy leading to an order of stability which is in good agreement with the conformer distribution determined by NMR investigations.

(16) For the synthesis of [1.1.1.1]paracyclophane see: Miyahara, Y.; Inazu, T.; Yoshino, T. *Tetrahedron Lett.* **1983**, *24*, 5277−5280. Sulfur analogue: Kaplan, M. L.; Reents, W. D. *Tetrahedron Lett* **1982**, *23*, 373−374.

(17) The activation energy of this process could not be derived from the spectra due to the incomplete separation of the signals even at −90 °C. For details see supporting information.

(18) (a) Typical extraction procedures use the colored metal salts of picric acid. The change in salt concentration by extration into the aqueous phase is measured photometrically. (b) Gokel, G. *Crown Ethers & Cryptands*, Monographs in Supramolecular Chemistry, Royal Society of Chemistry: Cambridge, 1991; pp 64−95.

(19) We thank Prof. Dr. M. Bahadir and M. Datsch, who made the technique available to us.

(20) (a) To give a rationale for the metal specificity of the macrocycles in the binding analysis, a more detailed structure investigation of the metal complexes by crystallography and in solution is necessary to determine effective pocket sizes and binding sites. (b) Compound **4a** does not show any significant metal extraction in the binding analysis.

(21) The authors have deposited atomic coordinates for **3a** and **3c** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. For details of the structures **3b** and **6** see ref 5.

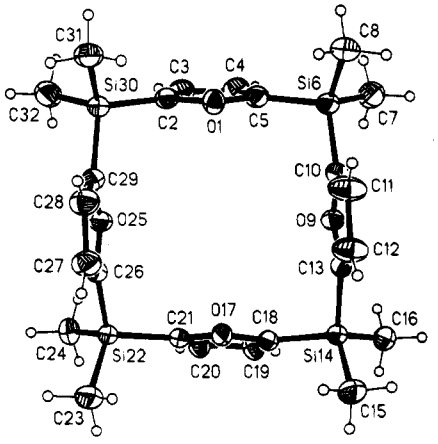


Figure 1. Crystal structure of **3a**.

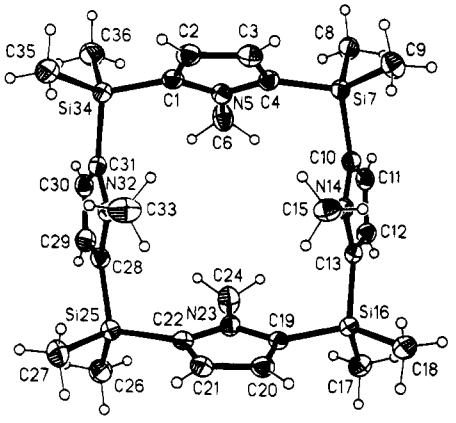


Figure 2. Crystal structure of **3c**.

crystal, similar to its known carbocyclic analogue tetrathiaporphyrinogen.[22]

Experimental Section

Melting points were taken on a hot-plate microscope apparatus and are not corrected. NMR spectra were recorded at 400 MHz (^{1}H) and 100 MHz (^{13}C) in chloroform-d solutions unless otherwise stated. The multiplicity of the ^{13}C signals was determined with the DEPT technique and quoted as: (+) for CH_3 or CH, (−) for CH_2 and (C_{quart}) for quarternary carbons.

General Procedure (GP 1) for the Synthesis of Sila-Hetero-Calixarenes 3a−f and 4a,b. To a suspension of 1.4 g (12 mmol) ^{t}BuOK in 300 mL of dry hexane at −60 °C was added 1.2 mL of *n*-BuLi (10 M in hexane) under nitrogen. The mixture was stirred for 10 min at −30 °C, 1.9 mL (12 mmol) of TMEDA and 6 mmol of the appropriate heterocycle were added, and the mixture was allowed to warm up to room temp in 1 h. A 730 μL (6 mmol) amount of Me_2SiCl_2 in 50 mL of dry hexane was slowly added by syringe pump (5 mL/h), the mixture was stirred for an 1 h and poured into 300 mL of water, and the organic layer was washed with two portions of water, dried over $MgSO_4$, and evaporated *in vacuo*. The crude products were purified by column chromatography on silica gel (CC) and crystallized from dichloromethane.

[1$_4$]Dimethylsila-2,5-furanocalixarene (3a) and [1$_6$]-Dimethylsila-2,5-furanocalixarene (4a). CC with CCl_4 yielded 120 mg (16%) of **3a** (R_f = 0.45, CCl_4) as colorless crystals: mp 115 °C; ^{1}H-NMR δ 0.53 (s, 24 H), 6.65 (s, 8 H); ^{13}C-NMR δ −3.2 (+), 120.4 (+), 161.8 (C_{quart}); IR (KBr, cm^{-1}) 2955, 1488, 1013; UV (CH_3CN, λ_{max} [log ε]) 192 (4.934), 248 (4.837); MS (70 eV), *m*/*z* (%) 496 (M$^+$, 100). Anal. Calcd for $C_{24}H_{32}O_4Si_4$: C 58.02, H 6.49. Found: C 58.38, H 6.60, and 75 mg (10%) of **4a** (R_f = 0.65, CCl_4) as a colorless oil: ^{1}H-NMR δ 0.55 (s, 36 H), 6.68 (s, 12 H); ^{13}C-NMR δ = −3.1 (+), 121.0 (+), 161.8 (C_{quart}); IR (KBr, cm^{-1}) 2955, 1488, 1013; UV (CH_3CN, λ_{max} [log ε]) 192 (4.933), 248 (4.835); MS (70 eV), *m*/*z* (%) 744 (M$^+$, 10), 207 (100). Anal. Calcd for $C_{36}H_{48}O_6Si_6$: C 58.02, H 6.49. Found: C 58.25, H 6.40.

[1$_6$]Dimethylsila-2,5-thiophenocalixarene (4b). CC with CCl_4 (or petroleum ether:ether 8:1) as eluent yielded two fractions: 154 mg (18%) of **3b**[5] (R_f = 0.4, CCl_4) and 146 mg (17%) of **4b** (R_f = 0.6, CCl_4), as a white solid, mp 290 °C; ^{1}H-NMR δ 0.62 (s, 36 H), 7.33 (s, 12 H); ^{13}C-NMR δ 0.0 (+), 136.5 (+), 143.8 (C_{quart}); IR (KBr, cm^{-1}) 2955, 1269, 1013, 811; UV (CH_3CN, λ_{max} [log ε]) 192 (4.934), 248 (4.837); MS (70 eV), *m*/*z* (%) 840 (M$^+$, 100). Anal. Calcd for $C_{36}H_{48}S_6Si_6$: C 51.37, H 5.75. Found: C 51.16, H 5.76.

[1$_4$]Dimethylsila-2,5(*N*-methylpyrrolocalixarene (3c). Recrystallization from CH_2Cl_2/hexane yielded 100 mg (12%) as a white solid: mp 295 °C; ^{1}H-NMR δ 0.44 (s, 24 H), 3.00 (s, 12 H), 6.41 (s, 8 H); ^{13}C-NMR δ −1.9 (+), 35.5 (+), 119.7 (+), 136.4 (C_{quart}); IR (KBr, cm^{-1}) 2958, 1483, 812; UV (CH_3CN, λ_{max} [log ε]) 194 (4.729), 246 (4.778), 258 (4.232); MS (70 eV), *m*/*z* (%) 548 (M$^+$, 20), 492 (100).

[1$_4$]Dimethylstanna-2,5-(*N*-methylpyrrolo)calixarene (3e). A 1.3 g (6 mmol) amount of Me_2SnCl_2 was used in the general procedure instead of Me_2SiCl_2. Recrystallization from CH_2Cl_2/hexane yielded 105 mg (8%) as a white solid: mp > 300 °C; ^{1}H-NMR δ 0.49 [t, ^3J (^{1}H, Sn) = 28.8 Hz, 24 H], 3.23 (s, 12 H), 6.42 [t, ^3J (^{1}H, Sn) = 5.6 Hz, 8 H]; ^{13}C-NMR δ −9.3 (+), 38.5 (+), 119.4 (+), 136.4 (C_{quart}); IR (KBr, cm^{-1}) 2925, 1345, 757; MS (70 eV), *m*/*z* (%): 908−916 (M$^+$, 40), 230 (100).

[1$_4$]Phenylphosphina-2,5-thiophenocalixarene (3f). A 760 mL (5.6 mmol) amount of freshly distilled dichlorophenylphosphine were used instead of Me_2SiCl_2 in the general procedure. CC (petroleum ether:diethyl ether 5:1) yielded 190 mg (17%) of **3f** (R_f = 0.42) as a white solid: mp 296 °C; ^{1}H-NMR δ 7.00 (m, 2 H), 7.25 (m, 20 H), 7.40 (m, 4 H), 7.70 (m, 2 H); ^{31}P-NMR (81 MHz) δ −30.14, −32.76; IR (KBr, cm^{-1}) 3053, 1585, 745; MS (70 eV), *m*/*z* (%) 760 (M$^+$, 100). Anal. Calcd for $C_{40}H_{28}S_4P_4$: C 63.15, H 3.71. Found: C 63.24, H 3.42.

Bis(5-*tert*-butyl-2-methoxyphenyl)dimethylsilane (6). A mixture of 16 g (100 mmol) of 4-*tert*-butylmethoxybenzene (**5**), 16.4 mL (110 mmol) of TMEDA, and 11 mL of *n*-BuLi (10 M) in 200 mL ether was stirred at room temp for 12 h, 6 mL (50 mmol) Me_2SiCl_2 was added, and the reaction mixture was stirred for additional 1 h. Usual workup, filtration through silica gel, and recrystallization from *n*-heptane yielded 16.2 g (84%) of **6** as large crystals: mp 106 °C; ^{1}H-NMR δ 0.52 (s, 6 H), 1.20 (s, 18 H), 3.65 (s, 6 H), 6.70 (m, 2 H), 7.30 (m, 4 H); ^{13}C-NMR δ −1.7 (+), 31.6 (+), 34.1 (C_{quart}), 55.1 (+), 109.0 (+), 125.7 (C_{quart}), 127.2 (+), 133.3 (+), 142.4 (C_{quart}), 162.3 (C_{quart}); IR (KBr, cm^{-1}) 2963, 1483, 818; UV (CH_3CN, λ_{max} [log ε]) 202 (4.861), 284 (3.728); MS (70 eV), *m*/*z* (%) 384 (M$^+$, 40), 369 (100). Anal. Calcd for $C_{24}H_{36}O_2Si$: C 74.94, H 9.43. Found: C 75.37, H 9.94.

Tetramethoxy-[1$_4$]dimethylsila-*p*-*tert*-butylcalixarene (7). To a solution of 2.3 g (6 mmol) of **6** and 2 mL (13 mmol) of TMEDA in 300 mL hexane was added 1.3 mL of *n*-BuLi (10 M in hexane) under nitrogen, and the mixture was stirred for 12 h at room temp. Next, 0.7 mL (6 mmol) of Me_2SiCl_2 in 50 mL of hexane was added over 7 h *via* syringe pump, the reaction mixture was poured into 300 mL of water and the organic layer was washed with water, dried, and evaporated *in vacuo*. Chromatography on silica gel (petroleum ether, 5% ether) gave 442 mg (16%) of **7** as a white solid: mp 160 °C; ^{1}H-NMR δ 0.46 (bs, 24 H), 1.12 (bs, 36 H), 3.00 (bs, 12 H), 7.36 (bs, 8 H); ^{13}C-NMR δ 0.4 (+), 31.4 (+), 31.5 (+), 34.3 (C_{quart}), 130.2 (C_{quart}), 135.1 (+), 144.6 (C_{quart}), 169.2 (C_{quart}); IR (KBr, cm^{-1}) 2963, 1389, 842; UV (CH_3CN, λ_{max} [log ε]) 204 (5.104), 286 (3.887); MS (70 eV), *m*/*z* (%) 880 (M$^+$, 20), 865 (M$^+$ − Me, 20), 57 (100). Anal. Calcd for $C_{52}H_{82}O_4Si_4$: C 69.43, H 9.19. Found: C 69.31, H 9.25.

Bis(2,3-dimethoxyphenyl)dimethylsilane (9). The analogous procedure as described for **6** yielded from 13 mL (100 mmol) of 1,2-dimethoxybenzene 15.5 g of **9** (93%) as a viscous

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oil; ^{1}H-NMR δ 0.59 (s, 6 H), 3.52 (s, 6 H), 3.83 (s, 6 H), 7.00 (m, 6 H); ^{13}C-NMR δ −0.7 (+), 56.2 (+), 60.8 (+), 114.7 (+), 124.6 (+), 127.8 (+), 133.3 (C_{quart}), 152.6 (C_{quart}), 154.5 (C_{quart}); IR (KBr, cm^{-1}) 2936, 1458, 1262; UV (CH_3CN, λ_{max} [log ϵ]) 204 (4.807), 282 (3.585); MS (70 eV) m/z (%) 332 (M^+, 11), 225 (100). Anal. Calcd for $C_{18}H_{24}O_4Si$: C 65.03, H 7.28. Found: C 64.97, H 7.27.

Octamethoxy-[1$_4$]dimethylsila-1,4-calixarene (10). The analogous procedure as described for **7** yielded from 2 g of **9** (6 mmol) 300 mg of crude **10** (12%), which was further purified by crystallization from dichloromethane to afford colorless crystals: mp 280 °C; ^{1}H-NMR δ 0.63 (s, 24 H), 3.58 (s, 24 H), 6.57 (s, 8 H); ^{13}C-NMR δ −1.2 (+), 59.4 (+), 130.5 (+), 135.2 (C_{quart})), 157.0 (C_{quart}); IR (KBr, cm^{-1}) 2905, 1376, 803; UV (CH_3CN, λ_{max} [log ϵ]) 208 (5.017), 224 (4.367), 288 (3.621); MS (70 eV) m/z (%) 776 (M^+, 40), 57 (100).

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (grant Ko 1537/1-1). Generous gifts of chemicals by the Degussa AG are gratefully acknowledged. B.K. thanks the Fonds der Chemischen Industrie for a Liebig stipend and Prof. Dr. H. Hopf for his support. We thank Ms. P. Schulz for recording the low temperature NMR spectra of **7** and **10**.

Supporting Information Available: ^{13}C NMR spectra of compounds **3c**, **3e**, and **10**, spectroscopic data of compounds **2c−f**, X-ray structure of **6**, low temperature ^{1}H NMR spectra of **10**, tables of the relative energies and geometrical parameters of the lowest energy conformers of **7**, crystal data of **3a** and **3c** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9512259