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Incorporation of Group 14 Elements into Siloxane-Bridged Paracyclophanes *cyclo*-[*p*,*p*′-$Me_2SiC_6H_4EMe_2C_6H_4SiMe_2O]_2$ (E = C, Si, Ge, Sn)[§]

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The bis(arylene silanes) *p*,*p*′-$HMe_2SiC_6H_4EMe_2C_6H_4SiMe_2H$ (E = C (**10**), Si (**11**), Ge (**12**), Sn(**13**)) were prepared by the in situ Grignard reaction of *p*,*p*′-$BrC_6H_4CMe_2C_6H_4Br$, Mg turnings, and $HSiMe_2Cl$ (for **10**) and the Grignard reaction using *p*-$HMe_2SiC_6H_4Br$, Mg turnings, and Me_2ECl_2 (E = Si for **11**, Ge for **12**, Sn for **13**). The oxidation of **10**–**13** using Pearlman's catalyst, $Pd(OH)_2/C$, in aqueous THF provided the bis(arylene silanols) *p*,*p*′-$HOMe_2SiC_6H_4EMe_2C_6H_4SiMe_2OH$ (E = C (**14**), Si (**15**), Ge (**16**), Sn(**17**)). The HCl-catalyzed condensation of **14**–**17** in highly diluted solutions of acetone/water afforded the siloxane-bridged paracyclophanes *cyclo*-[*p*,*p*′-$Me_2SiC_6H_4EMe_2C_6H_4SiMe_2O]_2$ (**6**–**9**) that incorporate the group 14 elements E = C, Si, Ge, and Sn. Compounds **6**–**17** were investigated by multinuclear solution and solid-state NMR spectroscopy and **6** and **9** also by X-ray crystallography.

Introduction

Silicon-bridged macrocycles[1] including silacyclophanes,[2] silacalixarenes,[3] silacalixquinones,[4] and silacrowns[5] have attracted considerable attention in recent years owing to their novel optical and electronic properties and applications in host–guest chemistry.

The first siloxane-bridged silacyclophanes, namely 2,4,6,8-tetrakis(dimethylsila)-3,7-dioxa-1,5(1,4)dibenzenacyclooctaphane (**1**) and 2,4,6,8-tetrakis(dimethylsila)-3,7-dioxa-1,5(1,3)dibenzenacyclooctaphane (**2**), were obtained as byproducts in extremely poor yields (4% and 6%, respectively), during the preparation of poly(tetramethyl-*para*-silaphenylenesiloxane)[6] and poly(tetramethyl-*meta*-silaphenylenesiloxane)[7] by the *n*-hexylamine 2-ethylhexoate-catalyzed polycondensation of *para*- and *meta*-bis(dimethylhydroxysilyl)benzene (Chart 1). Under more appropriate reaction conditions (e.g., high dilution, use of 4-(dimethylamino)pyridine as condensation catalyst) the yield of **2** was improved (43%) and its molecular structure determined by X-ray crystallography.[8] During the course of this work, a number of new siloxane-bridged silacyclophane derivatives, namely 2,4,6,8,9,11-hexakis(dimethylsila)-3,7,10-trioxa-1,5(1,3,5)dibenzenabicyclo[3.3.3]undecaphane (**3**), 2,4,6,8-tetrakis(dimethylsila)-3,7-dioxa-1,5(1,3)dithiophenacyclooctaphane (**4**), and 2,4,6,8-tetrakis(dimethylsila)-3,7-dioxa-1,5(1,3)dipyridinacyclooctaphane (**5**), were prepared via an alternative route and investigated by X-ray diffraction (Chart 1).[9] This route, which was also extended to the preparation of **1** and **2**, involves the hydrolytic polycondensation of arene precursors possessing two or three dimethylchlorosilyl groups and provides molecular products in fair to good yields (**1**: 28%, **2**: 65%: **3**: 15%, **4**: 7%, **5**: 62%).[9] In elegant work,

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[§] Dedicated to Professor Hans Hartl on the occasion of his retirement from The Free University of Berlin.

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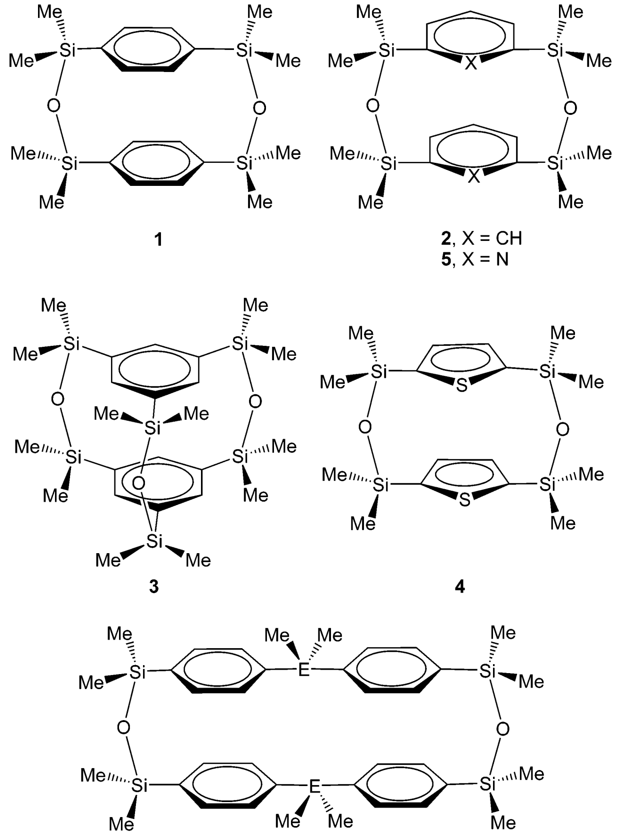
10.1021/om050265s CCC: \$30.25

Chart 1



1

2, X = CH
5, X = N

3

4

6, E = C **7**, E = Si
8, E = Ge **9**, E = Sn

the silacyclophane **1** as well as a phosphorus analogue of **5** were converted into their radical anions and fully characterized.[10] We now describe a rather mild route to a new class of siloxane-bridged paracyclophanes, *cyclo*-[p,p'-$\text{Me}_2\text{SiC}_6\text{H}_4\text{EMe}_2\text{C}_6\text{H}_4\text{SiMe}_2\text{O}]_2$ (**6**−**9**), that incorporate group 14 elements, E = C, Si, Ge, and Sn (Chart 1).

Discussion

The preparation of p,p'-$\text{HMe}_2\text{SiC}_6\text{H}_4\text{CMe}_2\text{C}_6\text{H}_4\text{SiMe}_2\text{H}$ (**10**) was achieved by adaptation of the in-situ Grignard method first reported in the 1960s (eq 1).[11] Bis(arylene silanes) p,p'-$\text{HMe}_2\text{SiC}_6\text{H}_4\text{EMe}_2\text{C}_6\text{H}_4\text{SiMe}_2\text{H}$ (E = Si (**11**), Ge (**12**), Sn(**13**)) were prepared using 2 equiv of the Grignard reagent derived from p-$\text{HSiMe}_2\text{SiC}_6\text{H}_4\text{Br}$ in reactions with Me_2SiCl_2, Me_2GeCl_2, and Me_2SnCl_2, respectively (eq 2). Compounds **10**−**13** were isolated by vacuum distillation in reasonable yields and obtained as colorless oils.

$$p,p'\text{-BrC}_6\text{H}_4\text{CMe}_2\text{C}_6\text{H}_4\text{Br} \xrightarrow[\text{HSiMe}_2\text{Cl}]{\text{Mg}} p,p'\text{-HMe}_2\text{SiC}_6\text{H}_4\text{CMe}_2\text{C}_6\text{H}_4\text{SiMe}_2\text{H} \quad (1)$$

10

$$2\ p\text{-HMe}_2\text{SiC}_6\text{H}_4\text{Br} + \text{Me}_2\text{ECl}_2 \xrightarrow{\text{Mg}} p,p'\text{-HMe}_2\text{SiC}_6\text{H}_4\text{EMe}_2\text{C}_6\text{H}_4\text{SiMe}_2\text{H} \quad (2)$$

11, E = Si
12, E = Ge
13, E = Sn

Bis(arylene silanols) p,p'-$\text{HOMe}_2\text{SiC}_6\text{H}_4\text{EMe}_2\text{C}_6\text{H}_4\text{SiMe}_2\text{OH}$ (**14**, E = C; **15**, E = Si; **16**, E = Ge; **17**, E = Sn) were obtained by the catalytic oxidation of the corresponding bis(arylene silanes) **10**−**13** in aqueous THF solutions using Pearlman's catalyst, $\text{Pd(OH)}_2\text{/C}$ (eq 3).[12] Compounds **14**−**17** were obtained as microcrystalline colorless solids in very good yields. Although organosilanols usually show a high degree of crystallinity,[13] all attempts to grow crystals suitable for X-ray crystallography failed. The number of magnetically inequivalent silicon atoms observed in the ^{29}Si MAS NMR spectra indicated that in all cases at least two independent molecules are present in the bulk materials.

$$p,p'\text{-HMe}_2\text{SiC}_6\text{H}_4\text{EMe}_2\text{C}_6\text{H}_4\text{SiMe}_2\text{H} \xrightarrow[\text{Pd(OH)}_2\text{/C}]{2\ \text{H}_2\text{O}} p,p'\text{-HOMe}_2\text{SiC}_6\text{H}_4\text{EMe}_2\text{C}_6\text{H}_4\text{SiMe}_2\text{OH} \quad (3)$$

10, E = C
11, E = Si
12, E = Ge
13, E = Sn

14, E = C
15, E = Si
16, E = Ge
17, E = Sn

The HCl-catalyzed condensation of highly dilute solutions of **14**−**17** in acetone/water provided the desired siloxane-bridged paracyclophanes *cyclo*-[p,p'-$\text{Me}_2\text{SiC}_6\text{H}_4\text{EMe}_2\text{C}_6\text{H}_4\text{SiMe}_2\text{O}]_2$ (**6**−**9**) as crystalline materials in reasonable to good yields (eq 4).[14] The ring size of **6**−**9** was established by osmometric molecular weight determinations (Chart 1).

$$p,p'\text{-HOMe}_2\text{SiC}_6\text{H}_4\text{EMe}_2\text{C}_6\text{H}_4\text{SiMe}_2\text{OH} \xrightarrow{\text{HCl cat.}} [p,p'\text{-Me}_2\text{SiC}_6\text{H}_4\text{EMe}_2\text{C}_6\text{H}_4\text{SiMe}_2\text{O}]_2 \quad (4)$$

14, E = C
15, E = Si
16, E = Ge
17, E = Sn

6, E = C
7, E = Si
8, E = Ge
9, E = Sn

The molecular structures of compounds **6** (E = C) and **9** (E = Sn) were established by X-ray crystallography and are shown in Figures 1 and 2; selected crystal data and bond parameters are collected in Tables 1 and 2. Both structures lie across a crystallographic center of inversion, which is consistent with the number of ^{29}Si MAS NMR signals. The intramolecular distances of the symmetry-related ring atoms, C1···C1a (9.5 Å) and Si2···Si2a (11.1 Å) for **6** and Sn1···Sn1a (10.5 Å) and Si2···Si2a (11.7 Å) for **9**, demonstrate that the cavities are nanosized, as opposed to compounds **1**−**4** (Figures 1 and 2). Although the structures are not isotypes, the 24-membered macrocycles of **6** and **9** adopt very similar conformations in the solid state. Differences were observed in the way compounds **6** and **9** are arranged in the crystal lattice. Molecules of **9** are packed in an eclipsed fashion, so that the overlaying cavities define

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(14) Several condensation catalysts under various reaction conditions were studied to maximize the yields of **6**−**9**. The most suitable conditions reported herein were adopted from: Omietanski, G. M. (Union Carbide Corporation) Patent No. 3,187,029, 1965.

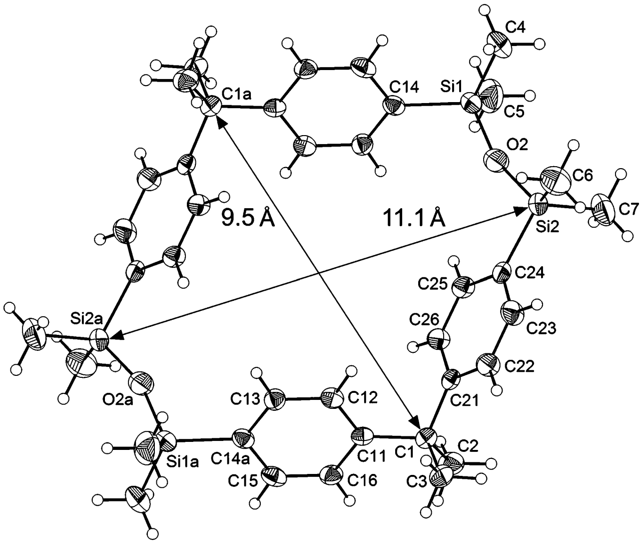

Figure 1. General view of **6** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Symmetry operation used to generate equivalent atoms: $a = 0.5 - x, 0.5 - y, 2 - z$.

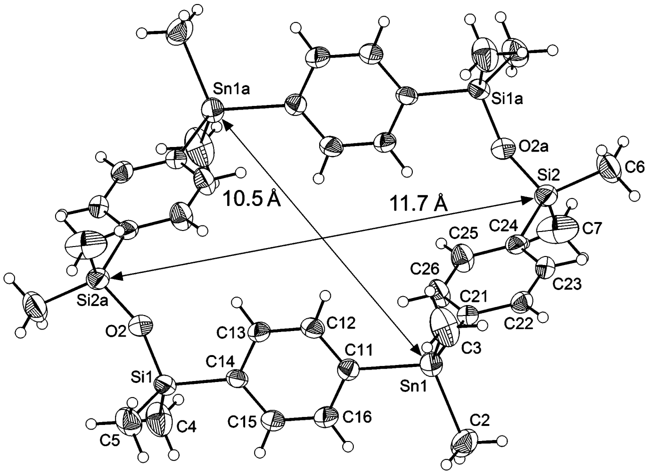

Figure 2. General view of **9** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Symmetry operation used to generate equivalent atoms: $a = -1 - x, 1 - y, -z$.

parallel running nanoporous channels in the crystal lattice (Figure 3), whereas no such channels were observed for compound **6**.

Conclusion

The present work describes a straightforward route to siloxane-bridged paracyclophanes, *cyclo*-[*p*,*p*′-$Me_2SiC_6H_4EMe_2C_6H_4SiMe_2O]_2$ (**6**−**9**), incorporating the group 14 elements E = C, Si, Ge, and Sn. Unlike the recently reported synthesis of compounds **3**−**5**, the preparation of **6**−**9** requires no harsh reagents, such as SO_2Cl_2, and the intermediates **10**−**17** are air-stable, as opposed to some intermediates in the preparation of **3**−**5**, which are moisture sensitive.[9] The shape and lengths of the organic/organometallic spacers made possible the preparation of siloxane-bridged paracyclophanes with nanoscale cavities and channels for the first time. We are currently investigating strategies to functionalize and cross-link **6**−**9** and related compounds to transfer them into potentially useful materials for applications in host−guest chemistry.

Table 1. Crystal Data and Structure Refinement for 6 and 9

	6	**9**
formula	$C_{38}H_{52}O_2Si_4$	$C_{36}H_{52}O_2Si_4Sn_2$
fw, g mol^{-1}	653.16	866.52
cryst syst	monoclinic	monoclinic
cryst size, mm	0.08 × 0.50 × 0.50	0.26 × 0.26 × 0.20
space group	*C*2/*c*	$P2_1/c$
a, Å	31.048(4)	7.1771(6)
b, Å	9.9074(12)	17.7623(16)
c, Å	12.6181(15)	17.1867(13)
α, deg	90	90
β, deg	91.957(3)	96.152(5)
γ, deg	90	90
V, Å^3	3879.1(8)	2178.4(3)
Z	4	2
ρ_{calcd}, Mg m^{-3}	1.118	1.321
T, K	293(2)	293(2)
μ, mm^{-1}	0.183	1.283
F(000)	1408	880
θ range, deg	1.3 to 25.0	3.2 to 27.5
index ranges	$-36 \leq k \leq 36$ $-11 \leq l \leq 11$ $-11 \leq h \leq 15$	$0 \leq k \leq 9$ $0 \leq l \leq 22$ $-22 \leq h \leq 22$
no. of reflns collcd	11 169	4942
completeness to θ_{max}	99.9%	99.0%
no. of indep reflns/R_{int}	3411	4942
no. of reflns obsd with $I > 2\sigma(I)$)	2350	2221
no. refined params	199	199
GooF (F^2)	1.039	0.758
$R_1(F)$ ($I > 2\sigma(I)$)	0.064	0.034
$wR_2(F^2)$ (all data)	0.148	0.088
$(\Delta/\sigma)_{max}$	<0.0001	<0.0001
largest diff peak/hole, e Å^{-3}	0.253/−0.277	0.432/−0.736

Table 2. Selected Bond Parameters [Å, deg] for 6 and 9[a]

6		**9**	
C1−C2	1.540(5)	Sn1−C2	2.128(5)
C1−C3	1.540(4)	Sn1−C3	2.106(5)
C1−C11	1.529(4)	Sn1−C11	2.111(6)
C1−C21	1.532(4)	Sn1−C21	2.128(5)
Si1−O2	1.611(3)	Si1−O2	1.603(3)
Si1−C4	1.849(5)	Si1−C4	1.842(5)
Si1−C5	1.841(4)	Si1−C5	1.843(5)
Si1−C14	1.856(3)	Si1−C14	1.855(5)
Si2−O2	1.615(3)	Si2−O2a	1.596(3)
Si2−C6	1.852(4)	Si2−C6	1.843(7)
Si2−C7	1.846(5)	Si2−C7	1.861(6)
Si2−C24	1.861(4)	Si2−C24	1.861(5)
C2−C1−C3	108.3(3)	C2−Sn1−C3	110.3(2)
C2−C1−C11	112.2(2)	C2−Sn1−C11	108.6(1)
C2−C1−C21	106.8(2)	C2−Sn1−C21	110.9(1)
C3−C1−C11	105.8 (2)	C3−Sn1−C11	111.6(1)
C3−C1−C21	112.6 (2)	C3−Sn1−C21	107.5(2)
C11−C1−C21	111.1(2)	C11−Sn1−C21	107.8(1)
O2−Si1−C4	109.1(2)	O2−Si1−C4	109.4(2)
O2−Si1−C5	109.0(2)	O2−Si1−C5	108.8(2)
O2−Si1−C14	108.3(1)	O2−Si1−C14	107.7(2)
C4−Si1−C5	111.4(2)	C4−Si1−C5	111.3(2)
C4−Si1−C14	110.3(2)	C4−Si1−C14	109.5(2)
C5−Si1−C14	108.7(2)	C5−Si1−C14	110.0(2)
O2−Si2−C6	110.6(2)	O2a-Si2−C6	110.3(2)
O2−Si2−C7	109.5(2)	O2a-Si2−C7	107.3(2)
O2−Si2−C24	106.8(1)	O2a-Si2−C24	108.2(2)
C6−Si2−C7	109.4(2)	C6−Si2−C7	111.5(2)
C6−Si2−C24	111.0(2)	C6−Si2−C24	110.1(2)
C7−Si2−C24	109.7(2)	C7−Si2−C24	109.5(2)
Si1−O2−Si2	160.3(2)	Si1−O2−Si2a	159.6(2)

[a] Symmetry operation used to generate equivalent atoms: $a = -1 - x, 1 - y, -z$.

Experimental Section

General Procedures. All solvents were distilled prior to use. 2,2′-Bis(*p*-bromophenyl)propane[15] and *p*-bromophenyldimethylsilane[16] were prepared according to known procedures. The commercial products $HSiMe_2Cl$, Me_2SiCl_2, Me_2GeCl_2, Me_2-

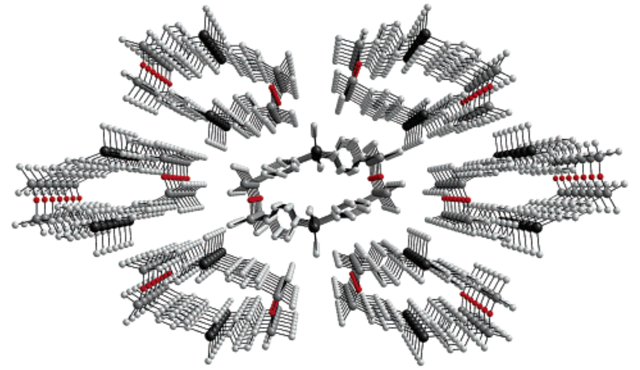

Figure 3. Perspective view of **9** along the crystallographic *a*-axis.

$SnCl_2$, and Pearlman's catalyst ($Pd(OH)_2/C$, 20 wt % (Pd dry basis) on carbon, water ≤ 50%) were purchased from Aldrich. The solution NMR spectra were measured using a JEOL Eclipse Plus 400 spectrometer (at 399.78 Mz (^1H), 100.54 (^{13}C), 79.42 (^{29}Si), and 149.05 (^{119}Sn)) and were referenced against $SiMe_4$ and $SnMe_4$. The solid-state NMR spectra were measured using the same instrument equipped with a 6 mm MAS probe. Crystalline $Si(SiMe_3)_4$ (δ_{iso} −9.9/−135.6) and *c*-Hex_4Sn (δ_{iso} −97.35) were used as secondary references. The ^{119}Sn MAS NMR spectra were obtained using cross polarization (contact time 5 ms, recycle delay 10 s). The IR spectra were recorded using a BioRad FTIR spectrometer. Microanalyses were carried out by CMAS, Belmont, Australia. Molecular weight determinations (c = 10.0 mmol; 40 °C; $CHCl_3$) were carried out using a Gonotec Osmomat 070 osmometer.

Synthesis of 2,2-Bis(*p*-dimethylsilylphenyl)propane (10). A solution of 2,2-bis(*p*-bromophenyl)propane (8.85 g, 25.0 mol) in THF (50 mL) was slowly added to an ice-cooled suspension of Mg turnings (2.43 g, 100 mmol) in THF (100 mL) and dimethylchlorosilane (9.46 g, 100 mmol). The reaction mixture was heated for 1 h at reflux, then poured into ice water (100 mL) and extracted with ether (2 × 100 mL). The combined organic extracts were dried over Na_2SO_4 and the volatiles removed under reduced pressure. The resultant oil was purified by Kugelrohr distillation.

10: yield 5.41 g, 17.3 mmol, 69%. Bp: 135 °C, 10^{-3} Torr. ^1H NMR ($CDCl_3$) δ: 7.53 (4H), 7.33 (4H), 4.45 (2H, $^1J(^1H-^{29}Si)$ = 188 Hz), 1.76 (6H), 0.41 (12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 151.5, 134.1, 133.8, 126.3, 42.9, 30.5, −3.8. $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ: −17.6. IR (neat, NaCl plates) ν_{SiH}: 2117 cm^{-1}. Anal. Calcd for $C_{19}H_{28}Si_2$ (312.60): C, 73.00; H, 9.03. Found: C, 72.96; H, 9.05.

Synthesis of Bis(*p*-dimethylsilylphenyl)dimethylsilane (11), -germane (12), and -stannane (13). To a Grignard solution, prepared from *p*-bromophenyldimethylsilane (32.3 g, 150 mol) and Mg turnings (7.29 g, 300 mmol) in THF (150 mL), was slowly added a solution of dimethylchlorosilane (6.45 g, 50.0 mmol) or dimethylgermanium dichloride (8.68 g, 50.0 mmol) or dimethyltin dichloride (11.0 g, 50.0 mmol) in THF (50 mL). The reaction mixture was heated for 12 h at reflux, then poured into ice water (200 mL) and extracted with ether (2 × 200 mL). The combined organic extracts were dried over Na_2SO_4 and the volatiles removed under reduced pressure. The resultant oil was purified by Kugelrohr distillation.

11: yield 7.56 g, 23.0 mmol, 46%. Bp: 150 °C, 10^{-3} Torr. ^1H NMR ($CDCl_3$) δ: 7.50 (8H), 4.39 (2H, $^1J(^1H-^{29}Si)$ = 188 Hz), 0.53 (6H), 0.31 (12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 139.1, 138.3, 133.6, 133.4, −2.5, −3.8. $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ: −7.7, −16.8. IR (neat, NaCl plates) ν_{SiH}: 2119 cm^{-1}. Anal. Calcd for $C_{18}H_{28}Si_3$ (328.67): C, 65.78; H, 8.59. Found: C, 66.62; H, 8.72.

12: yield 13.8 g, 37.0 mmol, 74%. Bp: 160 °C, 10^{-3} Torr. ^1H NMR ($CDCl_3$) δ: 7.86 (4H), 7.82 (4H), 4.79 (2H, $^1J(^1H-^{29}Si)$ = 189 Hz), 0.98 (6H), 0.66 (12 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 141.2, 137.6, 133.6, 133.1, −3.2, −3.8. $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ: −16.4. IR (neat, NaCl plates) ν_{SiH}: 2118 cm^{-1}. Anal. Calcd for $C_{18}H_{28}GeSi_2$ (373.22): C, 57.93; H, 7.56. Found: C, 57.82; H, 7.43.

13: yield 10.3 g, 24.5 mmol, 49%. Bp: 200 °C, 10^{-3} Torr. ^1H NMR ($CDCl_3$) δ: 7.70 (8H), 4.61 (2H, $^1J(^1H-^{29}Si)$ = 189 Hz), 0.66 (6H, $^2J(^1H-^{119}Sn)$ = 56 Hz), 0.51 (12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 141.8, 137.6, 135.7, 133.7, −3.8, −10.2 ($^1J(^{13}C-^{119}Sn)$ = 365 Hz). $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ: −17.0. $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ: −58.9. IR (neat, NaCl plates) ν_{SiH}: 2118 cm^{-1}. Anal. Calcd for $C_{18}H_{28}Si_2Sn$ (419.33): C, 51.56; H, 6.73. Found: C, 51.32; H, 6.71.

Synthesis of 2,2-Bis(*p*-dimethylhydroxysilylphenyl)propane (14) and Bis(*p*-dimethylhydroxysilylphenyl)dimethylsilane (15), -germane (16), and -stannane (17). To an ice-cooled suspension of Pearlman's catalyst (20 mg) in THF (50 mL) and water (5 mL) was slowly added a solution of **10** (3.12 g, 10.0 mmol), **11** (3.29 g, 10.0 mmol), **12** (3.73 g, 10.0 mmol), or **13** (4.19 g, 10.0 mmol) in THF (15 mL). After the evolution of hydrogen ceased, the reaction mixture was stirred at room temperature for 15 min. The catalyst was filtered off, the solvent was removed at 30 °C under reduced pressure, and ether (50 mL) was added to the residue. Most of the aqueous layer was removed with a pipet and the solution dried over Na_2SO_4. Hexane was added (20 mL) and two-thirds of the solvents removed at 30 °C under reduced pressure. Analytical pure products precipitated at −10 °C.

14: yield 3.07 g, 8.91 mmol, 89%. Mp: 142−143 °C. ^1H NMR ($CDCl_3$) δ: 7.49 (4H), 7.25 (4H), 1.69 (6H), 0.38 (12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 151.9, 135.9, 133.9, 126.3, 43.0, 30.4, −3.75. $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ: 8.1. $^{29}Si\{^1H\}$ MAS NMR δ_{iso}: 6.2, 5.8, 4.5, 3.4 (approximate ratio 1:1:1:1). IR (KBr) ν_{OH}: 3274 cm^{-1}. Anal. Calcd for $C_{19}H_{28}O_2Si_2$ (344.60): C, 66.22; H, 8.19. Found: C, 66.54; H, 8.22.

15: yield 3.07 g, 8.50 mmol, 85%. Mp: 114−116 °C. ^1H NMR ($CDCl_3$) δ: 7.55 (4H), 7.54 (4H), 0.54 (6H), 0.38 (12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 139.9, 139.6, 133.5, 132.3, −0.1, −2.6. $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ: 7.9, −8.0. $^{29}Si\{^1H\}$ MAS NMR δ_{iso}: 7.6, 5.9, −7.6, −10.0 (approximate ratio 1:3:1:1). IR (KBr) ν_{OH}: 3264 cm^{-1} Anal. Calcd for $C_{18}H_{28}O_2Si_3$ (360.68): C, 59.94; H, 7.82. Found: C, 59.79; H, 7.94.

16: yield 3.72 g, 9.15 mmol, 92%. Mp: 103−117 °C. ^1H NMR ($CDCl_3$) δ: 7.63 (4H), 7.57 (4H), 0.74 (6H), 0.41 (12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 141.6, 139.3, 133.0, 132.6, −0.1, −3.3. $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ: 7.6. $^{29}Si\{^1H\}$ MAS NMR δ_{iso}: 8.0, 6.5 (approximate ratio 1:3). IR (KBr) ν_{OH}: 3271 cm^{-1}. Anal. Calcd for $C_{18}H_{28}GeO_2Si_2$ (405.22): C, 53.35; H, 6.96. Found: C, 53.46; H, 7.09.

17: yield 2.39 g, 5.29 mmol, 53%. Mp: 99−111 °C. ^1H NMR ($CDCl_3$) δ: 7.61 (8H), 0.58 (6H), 0.41 (12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 142.3, 139.2, 135.7, 132.7, −0.12, −10.2 $^1J(^{13}C-^{119}Sn)$ = 365 Hz. $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ: 7.2. $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ: −59.3. $^{29}Si\{^1H\}$ MAS NMR 7.8, 6.0. $^{119}Sn\{^1H\}$ MAS NMR δ_{iso}: −57.1. IR (KBr) ν_{OH}: 3257 cm^{-1}. Anal. Calcd for $C_{18}H_{28}O_2Si_2Sn$ (451.33): C, 47.90; H, 6.25. Found: C, 47.82; H, 6.36.

Synthesis of 2,8-Bis(dimethyl)-4,6,10,12-tetrakis(dimethylsila)-5,11-dioxa-1,3,7,9(1,4)tetrabenzenacyclododecaphane (6), 2,4,6,8,10,12-Hexakis(dimethylsila)-5,11-dioxa-1,3,7,9(1,4)tetrabenzenacyclododecaphane (7), 2,8-Bis(dimethylgermana)-4,6,10,12-tetrakis(dimethylsila)-5,11-dioxa-1,3,7,9(1,4)tetrabenzenacyclododecaphane (8), and 2,8-Bis(dimethylstanna)-4,6,10,12-tetrakis(dimethylsila)-5,11-dioxa-1,3,7,9(1,4)tetrabenzenacyclododecaphane (9). A solution of **14** (1.72 g, 5.00 mmol), **15** (1.80 g, 5.00 mmol), **16** (2.03 g, 5.00 mmol), or **17** (2.26 g, 5.00 mmol) in acetone (350 mL) was diluted with water (50 mL) and concentrated HCl (10 μL) was added. The stoppered solution

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was left standing for 3 weeks. During this time a colorless precipitate formed, which was collected and air-dried. Recrystallization from hexane/dichloromethane afforded crystalline products.

6: yield 1.29 g, 1.97 mmol, 79%. Mp: 250−251 °C. ^{1}H NMR ($CDCl_3$) δ: 7.38 (4H), 7.17 (4H), 1.70 (6H), 0.41 (12H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 151.5, 136.5, 132.8, 126.1, 43.0, 30.7, 1.0. ^{29}Si{^{1}H} NMR ($CDCl_3$) δ: −1.6. ^{29}Si{^{1}H} MAS NMR δ_{iso}: −2.3, −2.7 (approximate ratio 1:1). Anal. Calcd for $C_{38}H_{52}O_2Si_4$ (653.18): C, 69.88; H, 8.02. Found: C, 69.90; H, 8.30. MW: 680 g mol^{-1}.

7: yield 497 mg, 0.73 mmol, 29%. Mp: 242−243 °C. ^{1}H NMR ($CDCl_3$) δ: 7.46 (8H), 0.53 (6H), 0.37 (12H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 140.4, 139.0, 133.4, 132.3, 0.9, −2.4. ^{29}Si{^{1}H} NMR ($CDCl_3$) δ: −8.0, −1.4. ^{29}Si{^{1}H} MAS NMR δ_{iso}: −2.0, −2.6, 6.6 (approximate ratio 1:1:1). Anal. Calcd for $C_{36}H_{52}O_2Si_6$ (685.33): C, 63.09; H, 7.65. Found: C, 63.15; H, 7.70. MW: 660 g mol^{-1}.

8: yield 1.28 g, 1.65 mmol, 66%. Mp: 243−245 °C. ^{1}H NMR ($CDCl_3$) δ: 7.55 (4H), 7.52 (4H), 0.71 (6H), 0.45 (12H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 141.2, 139.8, 133.0, 132.6, 43.0, 1.0, −3.1. ^{29}Si{^{1}H} NMR ($CDCl_3$) δ: −1.4. ^{29}Si{^{1}H} MAS NMR δ_{iso}: −2.2, −2.5 (approximate ratio 1:1). Anal. Calcd for $C_{36}H_{52}Ge_2O_2Si_4$ (774.42): C, 55.84; H, 6.77. Found: C, 55.80; H, 6.65. MW: 730 g mol^{-1}.

9: yield 719 mg, 0.83 mmol, 33%. Mp: 239−241 °C. ^{1}H NMR ($CDCl_3$) δ: 7.69 (4H), 7.48 (4H), 0.96 (6H, $^2J(^1H-^{119}Sn)$ = 58 Hz), 0.47 (12H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 139.7, 134.3, 132.9, 127.6, 0.8, −2.2. ^{29}Si{^{1}H} NMR ($CDCl_3$) δ: −1.1. ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ: −61.4. ^{29}Si{^{1}H} MAS NMR δ_{iso}: −2.0, −2.6 (approximate ratio 1:1).^{119}Sn{^{1}H} MAS NMR δ_{iso}: −59.1. Anal. Calcd for $C_{36}H_{52}O_2Si_4Sn_2$ (866.62): C, 49.89; H, 6.05. Found: C, 49.75; H, 5.95. MW: 880 g mol^{-1}.

Crystallography. Single crystals of **6** and **9** suitable for X-ray crystallography were obtained by evaporation from solutions of hexane/dichloromethane. Intensity data were collected on Bruker SMART Apex CCD (**6**) and Nonius Kappa CCD (**9**) diffractometers with graphite-monochromated Mo Kα (0.7107 Å) radiation. Data were reduced and corrected for absorption using the programs SAINT, SCALEPACK, and SADABS.[17,18] The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WinGX 2002.[19] Full-matrix least-squares refinement on F^2, using all data, was carried out with anisotropic displacement parameters applied to all nonhydrogen atoms. Hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically. The figures were created using DIAMOND.[20]

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-271653 (**6**) and CCDC-271652 (**9**). Copies of the information may be obtained free of charge from the The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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Supporting Information Available: Tables of all coordinates, anisotropic displacement parameters, geometric data and crystallographic data excluding structure factors (cif files) for **6** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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