Siloxa-bridged-cyclophanes featuring benzene, thiophene and pyridine units†

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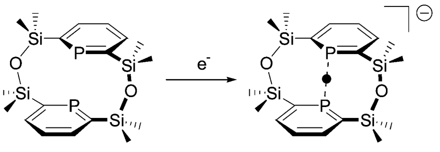
Two octamethyldisiloxa-bridged [3.3]cyclophanes (**1** and **2**) and a dodecamethyltrissiloxa-bridged [3.3.3]-cage compound (**3**) were prepared by hydrolysis of the chlorosilyl monomers. This general route was also employed for the preparation of two octamethyldisiloxa-bridged [3.3]heterophanes featuring two thiophene (**14**) or pyridine (**17**) moities.

Introduction

Since their discovery in 1949 by Brown and Farthing,[1] cyclophanes and their functional derivatives have been intensely studied. Their attractive geometry has been exploited in many different fields such as polymer science, biology, molecular recognition and organometallic chemistry.[2] Furthermore, it has long been known that small strained cyclophanes that allow π-stacking are well-suited materials for the study of electron transfer (ET) processes between aromatic structures.[3] In this regard, in 2001 we reported on the use of [3.3](2,6)phosphininophanes as a model for the ET process between phosphinine rings.[4] In that study we showed that the monoelectronic reduction of the siloxa-bridged [3.3](2,6)phosphininophane **I** resulted in the formation of a monoanionic species **II** featuring a one-electron phosphorus-phosphorus single bond (Scheme 1). This finding prompted us to enlarge this study to similar structures incorporating other types of aromatic rings. Herein, we report on the syntheses of siloxa-bridged cyclo- and heterophanes incorporating either benzene, thiophene or pyridine units.



I II

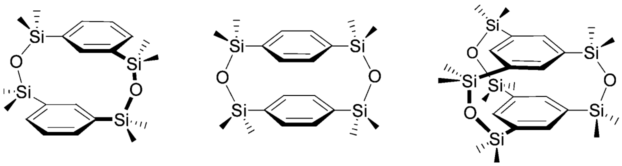
Scheme 1 Reduction of a diphosphacyclophane.

Results and discussion

Syntheses and X-ray analysis

A search of electronic databases indicated that three cyclophanes featuring two or three tetramethyldisiloxane groups as linkers were already known (shown in Scheme 2). The metacyclophane **1** was synthesized in 1999 by reacting 1,3-bis(dimethylhydroxysilyl)benzene with DMAP (overall yield of 21% from the 1,3-dibromobenzene).[5,6] The isomeric para derivative **2** was prepared in 1964 by thermal cracking of the corresponding poly(tetramethyl-*p*-silphenylsiloxane) polymer in the presence of NaOH at 300 °C and obtained with an overall yield of 2.6% from the 1,4-dibromobenzene. Unfortunately, no NMR or structural data for **2** are available.[7,8] Finally, the cage compound **3** was prepared by a two-step sequence from 1,3,5-tris(chlorodimethylsilyl)benzene.[9] The first step, which consists in a reductive self-coupling promoted by Na, furnished 1,2,9,10,17,18-hexasila[2.2.2](1,3,5)cyclophane featuring three Si–Si bonds with an extremely low yield of 0.22%. In a second step, oxidation of this cage-like phane with Et_3NO yielded macrocycle **3** in a nearly quantitative yield .

Various new synthetic approaches to cyclophanes **1**–**3** can be proposed. Among different possibilities, we deliberately favoured that which relies on coupling of the readily available Si–Cl derivatives with water. The general scheme of this approach is presented in Scheme 3. The first step consists in synthesis of the substituted 1,3-bis-, 1,4-bis- or 1,3,5-tris(ethoxydimethylsilyl)benzene derivatives **7**, **8** and **9**, obtained through a Grignard reaction from the corresponding bromoarene compounds **4**, **5** and **6**. The second step allows conversion of **7**–**9** into the respective chlorosilyl derivatives **10**–**12** using acetyl chloride. Compounds **10** and **11** have already been prepared by Tilley *et al.*[10] using the same sequence, and the 1,3,5-tris(chlorodimethylsilyl)benzene derivative **12** was obtained by Plenio by chlorination of the corresponding Si–H compound in CCl_4.[11] Though the tris(ethoxydimethylsilyl) derivative **9** could not be obtained in pure form (90% purity), we found our approach much more convenient since it avoids the use



1 2 3

Scheme 2 Three siloxa-bridged cyclophanes.

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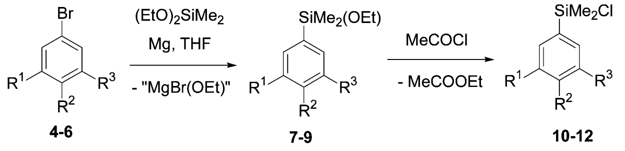
† Electronic supplementary information (ESI) available: crystal data and X-ray structure of [3.3](1,4)cyclophane (**2**). See http://www.rsc.org/suppdata/nj/b2/b211045h/



	4	5	6	7	8	9	10	11	12
R^1	Br	H	Br	$SiMe_2(OEt)$	H	$SiMe_2(OEt)$	$SiMe_2Cl$	H	$SiMe_2Cl$
R^2	H	Br	H	H	$SiMe_2(OEt)$	H	H	$SiMe_2Cl$	H
R^3	H	H	Br	H	H	$SiMe_2(OEt)$	H	H	$SiMe_2Cl$

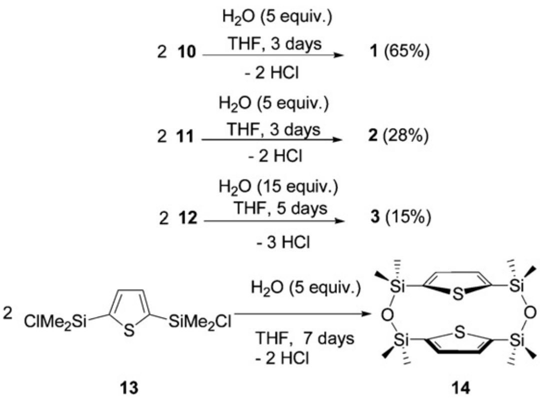
Scheme 3 Synthetic strategy.

of chlorine. Compound **12** was obtained after reaction of **9** with acetyl chloride with a nearly quantitative yield.

Syntheses of the respective macrocycles **1**–**3** (Scheme 4) were conducted in THF at room temperature in the presence of water. As expected, we found that dilution and the amount of water used played a crucial role in the cyclization process and many experiments were carried out to determine the best experimental conditions. In all cases, the use of high concentrations resulted exclusively in the formation of polymers whose compositions were not determined. Using a rather high dilution (between 7 and 11.4 mmol L^{-1}) and an excess of water (5 equiv. for **1** and **2** and 15 equiv. for **3**) the expected macrocycles were formed in modest to good yields. Nevertheless, in all cases these yields were found to be higher than those previously reported. Cyclophane **1** was obtained with a yield of 65% (36% from 1,3-dibromobenzene). On the other hand, the paracyclophane **2** was isolated with an overall yield of 28% (17.3% from the 1,4-dibromobenzene). This compound was fully characterized by NMR techniques (^{1}H and ^{13}C), elemental analyses and its formulation was definitely ascertained by X-ray crystallography (given in the Electronic supplementary information, ESI).

In compound **2**, the two benzene rings do not lie exactly above one another, as was also reported for [3,3]paracyclophane.[12] The inter-ring distance is 3.607 Å. The most significant structural feature concerns the Si–C bonds, which deviate from the planes defined by the two rings (Θ between 7° and 9°). This distorsion, observed for [3.3]paracyclophane too, shows that a substantial cyclic strain exists in **2**.

The most significant synthetic improvement was obtained in the synthesis of cyclophane **3**, which was isolated with an overall yield of 15%. This macrocycle was also fully identified by NMR spectroscopy, by comparison with reported data, elemental analyses and its X-ray structure was recorded (shown in Fig. 1).[9] At 3.503 Å, the inter-ring distance is slighly shorter than that in the paracyclophane **2**. As noted above for **2**, though the two aromatic rings are roughly planar the three Si–C(ring) bonds significantly deviate from the mean planes defined by the rings (Θ between 5° and 7°). Apart from this, the structure of **3** does not deserve special comments and bond lengths within the ring fall in the usual range (see Table 1).



Scheme 4 Synthesis of cyclophanes **1**, **2** and **3** and [3,3]thiophenophane **14**.

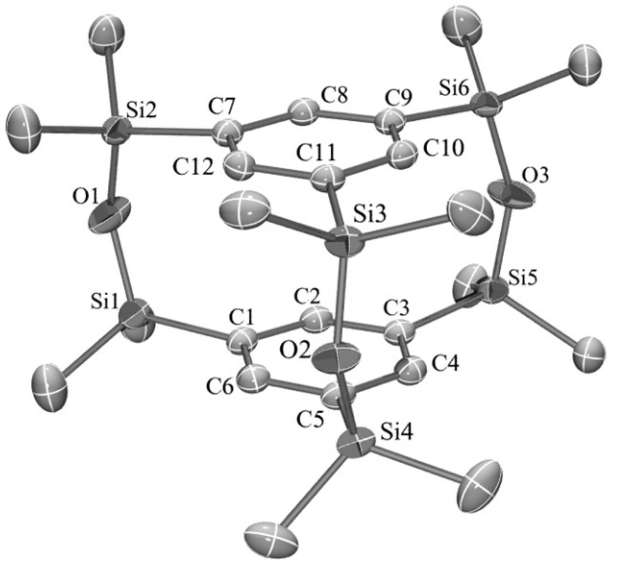


Fig. 1 ORTEP view of one molecule of **3**. The numbering is arbitrary and different from that used in the ^{13}C NMR spectrum. All hydrogen atoms have been deliberately omitted for clarity.

These first encouraging results prompted us to investigate the synthesis of similar siloxa-bridged heterophanes incorporating thiophene and pyridine units. The strategy employed slightly differs from that depicted above in that the synthesis of 2,5-bis(chlorodimethylsilyl)thiophene was not realized using the same Grignard-mediated approach. Two routes have already been reported for the synthesis of **13**: an electrochemical method that involves the coupling[13] between 2,5-dibromothiophene and Me_2SiCl_2 and a palladium-mediated route that relies on the coupling of the 2,5-bis(dimethylsilyl)thiophene with CCl_4.[14] We found that the trapping reaction of the readily available 2,5-dilithiothiophene with Me_2SiCl_2 is a more straightforward approach.

Having this compound in hand, synthesis of the thiophenophane derivative **14** could be achieved (Scheme 4), albeit in a very low yield that could not be improved despite many attempts. This new cyclophane was successfully characterized by NMR techniques, elemental analyzes and its formulation was further confirmed by an X-ray crystallographic study (selected parameters given in Table 2). In the solid state, **14** adopts an *anti* conformation (Fig. 2), the two thiophene rings defining two roughly parallel planes that are separated by 3.15 Å. As noted above in the structures of **2** and **3**, a cyclic strain is also visible in **14** since the Si–C bonds are not coplanar with the two ring planes (Θ between 5° and 9°).

Preparation of the siloxa-bridged pyridinophane **17** also constituted an interesting goal. 2,6-Bis(bromodimethylsilyl)-pyridinium bromide (**15**) was selected as precursor. In 1992, Plenio had devised a very convenient route to this salt, which relies on trapping of 2,6-dimagnesiopyridine with Me_2SiHCl,

Table 1 Selected bond lengths (Å) and angles (deg) for compound **3**

C(1)–C(2)	1.404(2)	Si(1)–O(1)–Si(2)	148.68(8)
C(2)–C(3)	1.399(2)	O(1)–Si(1)–C(1)	109.47(6)
C(3)–C(4)	1.400(2)	C(2)–C(1)–Si(1)	120.9(1)
C(4)–C(5)	1.393(2)	C(6)–C(1)–Si(1)	121.9(1)
C(5)–C(6)	1.403(2)	C(6)–C(1)–C(2)	117.1(1)
C(1)–C(6)	1.399(2)	C(3)–C(2)–C(1)	122.8(1)
Si(1)–C(1)	1.877(1)		
Si(1)–O(1)	1.633(1)		

Table 2 Selected bond lengths (Å) and angles (deg) for compound **14**

S(1)–C(1)	1.723(2)	C(1)–S(1)–C(4)	94.42(8)
C(1)–C(2)	1.371(2)	C(2)–C(1)–S(1)	108.9(1)
C(2)–C(3)	1.417(2)	O(1)–Si(1)–C(4)	109.28(6)
C(3)–C(4)	1.376(2)	Si(1)–O(1)–Si(2)	144.48(7)
C(4)–S(1)	1.724(2)	C(1)–C(2)–C(3)	114.2(1)
Si(1)–C(4)	1.862(2)	C(4)–C(3)–C(2)	113.6(1)
Si(2)′–C(1)	1.866(2)	C(3)–C(4)–S(1)	108.9(1)
Si(1)–O(1)	1.636(1)	C(3)–C(4)–Si(1)	126.9(1)
Si(2)–O(1)	1.644(1)	S(1)–C(4)–Si(1)	123.9(1)

followed by a Si–H to Si–Br exchange using bromine.[11] Hydrolysis of **15** was carried out in THF despite the low solubility of the salt and the desired bispyridinium macrocycle **16** was isolated in very good yield (80%).

This new pyridinophane, which was found to be insoluble in most common organic solvents and only sparingly soluble in MeCN, was fully characterized by NMR techniques and elemental analyses. Though the two acidic protons could not be detected in the ^{1}H NMR spectrum of **16**, the formation of the salt was clearly apparent from the downfield shifts of the H_4 protons, which appear as a triplet at $\delta(CD_3CN) = 8.48$ ppm with $^3J(H\text{–}H) = 7.8$ Hz. However, a final proof of the structure was given by X-ray crystallography. An ORTEP view of one molecule of **16** is presented in Fig. 3 and selected geometrical parameters in Table 3. In the solid state, **16** adopts a *syn* conformation, as shown in Scheme 5, but there is no steric hindrance between the two pyridinium protons, which lie 2.584 Å apart.

Conversion of **16** into the neutral pyridinophane **17** proved to be problematic and many combinations of bases and solvents were tested without success. Finally we found that direct abstraction of the two acidic protons with MeLi as a base in hexane at 0 °C proved to be the most convenient way to generate **17** (Scheme 5). Using this simple approach, **17** could be isolated pure by simple filtration of the LiBr salt with a very good yield (78%). Compound **17**, which turned out to be slightly moisture sensitive, was successfully characterized by means of NMR spectroscopy and elemental analyses. Unfortunately, no structural information could be gained and all our attempts to crystallize **17** have failed so far.

Dynamic ^{1}H NMR study

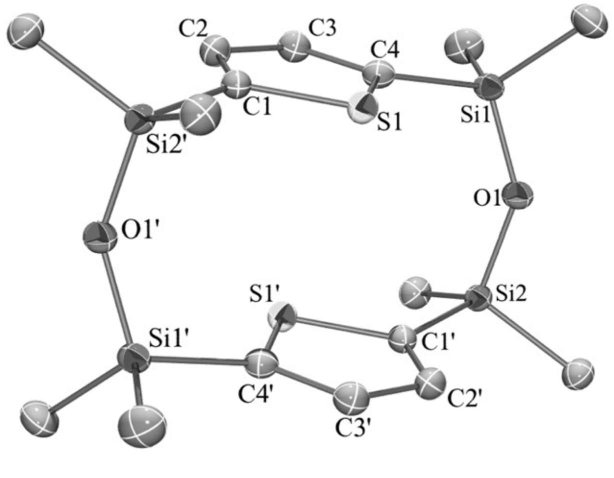


Fig. 2 ORTEP view of one molecule of **14**. The numbering is arbitrary and different from that used in the ^{13}C NMR spectrum. All hydrogen atoms have been deliberately omitted for clarity.

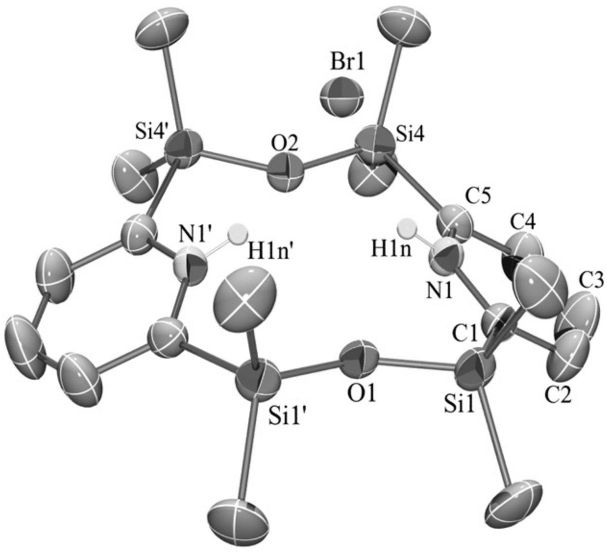


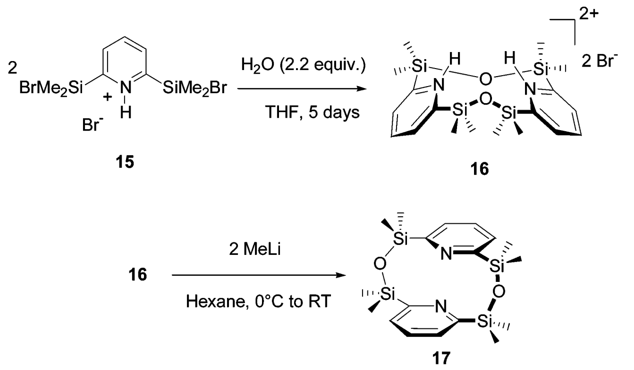
Fig. 3 ORTEP view of one molecule of **16**. The numbering is arbitrary and different from that used in the ^{13}C NMR spectrum. All hydrogen atoms, except those bound to nitrogen atoms, as well as one of the two bromide counteranions, have been deliberately omitted for clarity.

[3.3]Metacyclophanes can adopt two conformations, *syn* and *anti*, and the preference for one of the two is strongly dependent on the length of the connecting chains and on the substitution pattern of the cyclophane. For instance, [2.2]- and [3.4]cyclophane and derivatives adopt the *anti* conformation whereas [3.3]metacyclophane adopts the *syn* conformation.[15] Shinmyozu *et al.* and Semmelhack *et al.* showed that dynamic NMR experiments could give precious conformational information for this type of macrocycles.[15,16] First, they proved that the barrier to aromatic nucleus inversion between *syn* and *anti* is very low (no freezing of the process down to 180 K). Secondly, when the *syn* conformation is favoured, bridge-isomerization between *syn*(chair-chair), *syn*(chair-boat) and *syn*(boat-boat) becomes observable (Scheme 6). A 48.5 kJ mol^{-1} barrier between conformers *syn*(chair-chair) and *syn*(chair-boat) was observed in the case of d_4-[3.3]metacyclophane.[15]

Subsequent studies in which methylene moieties of the bridge were replaced by NH, S or Se and/or pyridine was substituted by benzene led to the same type of results, namely, fast inversion of the preferred *syn* geometry and slower bridge isomerization.[16,17] It was thus interesting to study the variable temperature NMR for the metacyclophanes reported in this article, especially in the case of pyridinophane **17** whose conformation was unknown. As noted above, the crystal structure for cyclophanes **1** and **14** revealed a preferred *anti* conformation. Dynamic ^{1}H NMR studies on these two species confirmed that this geometry is also preferred in solution. Indeed, we could not detect the freezing of the ring inversion down to 180 K. The same experiment was conducted on compound **17** and the spectra can be seen in Fig. 4. The CH_3 groups are equivalent at room temperature and down to 208 K. They split into two singlets (one for the axial group and

Table 3 Selected bond lengths (Å) and angles (deg) for compound **16**

N(1)–C(1)	1.353(4)	C(5)–N(1)–C(1)	126.7(3)
N(1)–C(5)	1.351(4)	N(1)–C(1)–C(2)	116.0(3)
N(1)–H(1N)	.82(4)	N(1)–C(1)– Si(1)	120.2(3)
C(1)–C(2)	1.382(5)	C(2)–C(1)–Si(1)	123.8(3)
C(2)–C(3)	1.368(6)	C(3)–C(2)–C(1)	120.7(4)
C(3)–C(4)	1.376(6)	C(2)–C(3)–C(4)	120.8(4)
C(4)–C(5)	1.398(5)	C(3)–C(4)–C(5)	119.7(4)
Si(1)–O(1)	1.634(2)	N(1)–C(5)–C(4)	116.0(4)
Si(1)–C(1)	1.901(4)		



Scheme 5 Synthesis of the pyridinium-based cyclophane **16** and [3,3]pyridinophane **17**.

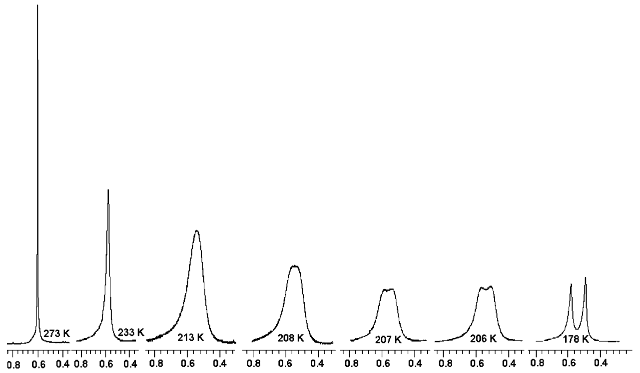


Fig. 4 Variable temperature NMR spectra (in ppm) of compound **17** in CD_2Cl_2.

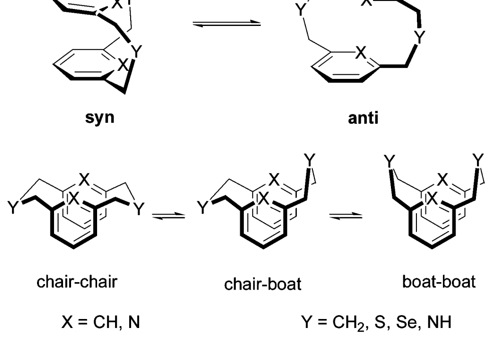
one for the equatorial) upon further lowering of the temperature. This clearly indicates that what we observe is a *syn*-(chair-chair) to *syn*(chair-boat) to *syn*(boat-boat) bridge interconversion. From the NMR data we could extract an activation barrier for this interconversion of 43.2 kJ mol^{-1},[18] which is consistent with what was previously observed for such a process.[17]

In conclusion, we have developed a new route for the synthesis of three siloxa-bridged cyclophanes relying on the direct coupling of Si–Cl derivatives with water. In all cases, this new procedure proved to be much more convenient than those reported so far, especially for preparation of the cage compound **3**. Though the yield still remains modest, this improvement should now allow the host–guest properties of this new edifice to be explored. Additionally, this new synthetic approach was employed to prepare two new siloxa-bridged [3.3]heterophanes incorporating thiophene or pyridine units.

Experimental

General

All reactions were routinely performed under an inert atmosphere of nitrogen by using Schlenk and glove-box techniques and dry deoxygenated solvents. Dry THF and hexanes were obtained by distillation from Na/benzophenone and dry CH_2Cl_2 and $CDCl_3$ from P_2O_5. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz for ^1H, 75.5 MHz for ^{13}C. Solvent peaks are used as internal reference relative to Me_4Si for ^1H and ^{13}C chemical shifts (ppm) and coupling constants are expressed in Hertz. The following abbreviations are used: b; broad, singlet; d, doublet; t, triplet; m, multiplet. Mass spectra were obtained at 70 eV with an HP 5989B spectrometer coupled to an HP 5980 chromatograph by the direct inlet method. Elemental analyses were performed by the "Service d'Analyse du CNRS" at Gif sur Yvette, France.



Scheme 6 The two dynamical processes in [3,3]metacyclophanes.

Syntheses

1,1,3,3,10,10,12,12-Octamethylsil-2,11-oxa[3.3](1,3)cyclophane (1). 1,3-Bis(chlorodimethylsilyl)benzene (**10**; 1.5 g, 5.7 mmol) was dissolved in THF (200 mL) and water (0.5 mL, 27.8 mmol) was added in one portion at room temperature. The resulting solution was stirred for 3 days and the solvent was evaporated. The white solid obtained was then successively washed with ether (2 × 10 mL) and hexane (2 × 20 mL). After drying, cyclophane **1** was obtained as a white powder. Yield: 0.77 g (65%); mp 208 °C. For spectroscopic characterizations, see ref. 5.

1,1,3,3,10,10,12,12-Cctamethylsilyl-2,11-oxa[3.3](1,4)cyclophane (2). 1,4-Bis(chlorodimethylsilyl)benzene (**11**; 0.90 g, 3.40 mmol) was dissolved in THF (500 mL) and water (0.310 mL, 17.2 mmol) was added in one portion at room temperature. The resulting solution was stirred for 3 days and the solvent was evaporated. After washing with ether (20 mL) and hexanes (20 mL), macrocycle **2** was isolated as a white powder. Yield 0.20 g (28%); mp 208 °C. ^1H NMR ($CDCl_3$): δ 0.37 (24H, s, $SiMe_2$), 7.00 (s, 8H, H of C_6H_4); ^{13}C $\{^1H\}$ NMR ($CDCl_3$): δ 0.5 (s, $SiMe_2$), 132.3 (s, CH of C_6H_4), 138.8 (s, C_{ipso} of C_6H_4). MS (*m*/*z*, %): 417 (M, 100). Anal. calcd for $C_{20}H_{32}O_2Si_4$: C, 57.63; H, 7.74; found: C, 57.34; H, 7.39%.

1,1,3,3,10,10,12,12,19,19,21,21-Dodecamethylsilyl-2,11,20-oxa-[3.3.3](1,3,5)cyclophane (3). 1,3,5-Tris(chlorodimethylsilyl)benzene (**12**; 5.00 g, 14 mmol) was dissolved in THF (2 L) and water (4 mL, 222 mmol) was added in one portion at room temperature. The resulting solution was stirred for 5 days and then evaporated to dryness. The orange oil obtained was subjected to chromatography on silica gel using hexane as solvent. After having eluted a first fraction that mainly contained polymeric materials and traces of **3**, the macrocycle was obtained in a second fraction ($R_f = 0.13$, SiO_2, hexane). **3** was recovered as a yellow powder after evaporation of solvents. Yield: 585 mg (overall 15%). For spectroscopic characterizations, see ref. 9.

1,3,5-Tris(ethoxydimethylsilyl)benzene (9). Bis(ethoxy)dimethylsilane (40.8 mL, 238 mmol), magnesium (6.9 g, 287.5 mmol) and THF (200 mL) were placed into a 500 mL flask under nitrogen. The resulting mixture was heated at 50 °C and a solution of tribromobenzene (**6**; 25.0 g, 79.4 mmol) in THF (70 mL) was added dropwise (duration: 3 h). The solution was then heated for 25 h under reflux. After cooling to room temperature, the solution was filtered. After evaporation of the solvent, the brown oil obtained was extracted twice with hexane (2 × 30 mL) to yield an orange oil. This oil did not

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contain exclusively **9** and traces of 1,3-bis(ethoxydimethylsilyl)benzene were detected in the ^{1}H and ^{13}C NMR spectrum (between 5 to 8%). Unfortunately, further attempts to purify **9** by distillation led to a partial decomposition of the compound. Yield: 19 g (62%). ^{1}H NMR ($CDCl_3$): δ 0.41 (s, 18 H, $SiMe_2$), 1.21 [t, 9 H, ^3J(H–H) = 6.98, Me], 3.71 [q, 6 H, ^3J(H–H) = 6.98, OCH_2], 7.85 (s, 3 H, H of C_6H_3). ^{13}C {^{1}H} NMR ($CDCl_3$): δ −1.6 (s, $SiMe_2$), 18.5 (s, Me of OEt), 58.8 (s, OCH_2), 136.3 (s, $C_{1,3,5}$ of C_6H_3), 139.8 (s, CH of C_6H_3). MS: m/z (%): 384 (2) [M – 1], 368 (100) [$M - CH_3$], 324 (20) [$M - CH_3 - OC_2H_5$], 281 (18) [$M - Si(CH_3)_2OC_2H_5$], 267 (40) [$M - Si(CH_3)_2OC_2H_5 - CH_3$], 177 (60) [$M - 2\,Si(CH_3)_2OC_2H_5$].

1,3,5-Tris(chlorodimethylsilyl)benzene (12). Compound **9** (5 g, 13 mmol) and acetyl chloride (10 mL), which was used both as reagent and solvent, were heated at 80 °C for 15 h. After evaporation of the excess acetyl chloride and ethyl acetate, compound **12** was recovered as a brownish oil. After distillation, **12** was recovered as a colourless oil (purity 95%). Yield: 4.62 g ($>$ 99%). For spectroscopic charcaterizations, see ref. 11.

2,5-Bis(chlorodimethylsilyl)thiophene (13). The 2,5-bis(chlorodimethylsilyl)thienyl derivative was obtained through the reaction of the dilithium salt with Me_2SiCl_2 in excess. A solution of butyllithium (1.6 M in hexane; 40 mmol, 25 mL) was added dropwise at room temperature to a solution of thiophene (1.64 g, 20 mmol) and TMEDA (4.64 g, 40 mmol). The resulting mixture was then heated under reflux for 90 min. After cooling to −20 °C, Me_2SiCl_2 (51.84 g, 400 mmol) was added and the resulting solution was heated under reflux for 2 h. After evaporation of the excess Me_2SiCl_2, the orange residue obtained was distilled. Compound **13** was recovered as a colourless oil. Yield: 3.77 g (70%). For spectroscopic characterizations, see ref. 14.

1,1,3,3,9,9,11,11-Octamethylsilyl-2,10-oxa[3.3](2,5)thiophenophane (14). **13** (4 g, 15 mmol) was dissolved in THF (1.5 L) and water (1.35 g, 65 mmol) was added in one portion at room temperature. The resulting solution was stirred for 1 week. After evaporation of the solvent, the orange residue obtained was crystallized in methanol (10 mL) at room temperature. After filtration, compound **14** was recovered as a white solid. Yield: 0.20 g (7%); mp 175 °C. ^{1}H ($CDCl_3$): δ 0.36 (s, 24H, $4 \times SiMe_2$), 7.26 (s, 4H, H of C_4H_2S). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 0.3 (s, $SiMe_2$), 134.1 (s, CH of C_4H_2S), 158.1 (s, C_{ipso} of C_4H_2S). MS (m/z, %): 429 (M, 100). Anal. calcd for $C_{16}H_{28}O_2S_2Si_4$: C, 44.81; H, 6.58; found: C, 44.70; H, 6.63%.

Precursor 16. The 2,6-bis(bromodimethylsilyl)pyridine hydrobromide salt (**15**; 5 g, 11.5 mmol) was dissolved in THF (700 mL) and water (0.4 g, 22.2 mmol) was added in one portion at room temperature. After 5 days of stirring, macrocycle **16** was collected by filtration and washed with ether (20 mL). After drying, **16** was recovered as a white solid. Yield: 2.66 g (80%); mp $>$ 260 °C. ^{1}H NMR (CD_3CN): δ 0.88 (s, 24H, $SiMe_2$), 8.19 [dd, 4 H, ^3J(H–H) = 7.8 Hz, ^4J(H–H) = 1.3 Hz, H_3 of C_5H_3N], 8.48 [t, 2 H, ^3J(H–H) = 7.8, H_4 of C_5H_3N]. ^{13}C {^{1}H} NMR (CD_3CN): δ 0.0 (s, $SiMe_2$), 134.0 (s, C_3 of C_5H_3N), 143.5 (s, C_4 of C_5H_3N), 160.3 (s, C_2 of C_5H_3N). MS (m/z, %): 419 (100) [M – 1], 282 (75) [$M - C_5H_5NSiMe_2$]. Anal. calcd for $C_{18}H_{32}Br_2N_2O_2Si_4$: C, 37.24; H, 5.56; found: C, 37.30; H, 5.65%.

1,1,3,3,10,10,12,12-Octamethylsilyl-2,11-oxa[3.3](2,6)pyridinophane (17). Compound **16** (0.30 g, 0.519 mmol) was suspended in hexane (15 mL). Methyllithium in ether (1.6 M; 0.66 mL, 1.056 mmol) was then added to this solution at 0 °C. After warming up to room temperature, the solution was stirred at room temperature for 3 h. After evaporation of the solvent, dichloromethane was added and the resulting solution was filtered on celite. The pink powder obtained was successively washed with hexane (5 mL) and Et_2O (2 × 5 mL), after evaporation of the solvent. After drying, pyridinophane **17** was recovered as a slightly coloured pink solid. Yield: 0.17 g (78%); mp $>$ 260 °C. ^{1}H NMR ($CDCl_3$): δ 0.61 (s, 24H, $SiMe_2$), 7.4 [d, 4 H, ^3J (H–H) = 7.6 Hz, H_3 of C_5H_3N], 7.65 [t, 2 H, ^3J (H–H) = 7.8 Hz, H_4 of C_5H_3N]. ^{13}C {^{1}H} NMR ($CDCl_3$): δ 0.6 (s, $SiMe_2$), 127.7 (s, C_3 of C_5H_3N), 132.8 (s, C_4 of C_5H_3N), 171.23 (s, C_2 of C_5H_3N). MS (m/z, %): 429 (M, 100). Anal. calcd for $C_{18}H_{30}N_2O_2Si_4$: C, 51.62; H, 7.22; found: C, 51.50; H, 7.29%.

Table 4 X-Ray data and structural refinement details for compounds **3**, **14** and **16**

Compound	**3**	**14**	**16**
Molecular formula	$C_{24}H_{42}O_3Si_6$	$C_{16}H_{28}O_2S_2Si_4$	$C_{18}H_{32}Br_2N_2O_2Si_4 \cdot C_4H_8O$
FW	547.12	428.86	652.74
T/K	150.0(10)	150.0(10)	150.0(10)
λ/Å	0.71069	0.71069	0.71069
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	P^-1	$Pnma$
a/Å	17.0411(3)	6.7411(2)	23.444(5)
b/Å	12.0953(2)	8.2744(2)	12.699(5)
c/Å	16.9900(2)	11.44040(10)	10.521(5)
α/deg	90.00	72.939(2)	90.00
β/deg	114.0700(10)	72.984(2)	90.00
γ/deg	90.00	73.3800(10)	90.00
U/Å^3	3197.43(9)	569.18(2)	3132(2)
Z	4	1	4
μ(MoKα)/cm^{-1}	0.283	0.452	2.765
Reflect. measured	15394	4544	6591
Indep. reflect.	9244	3296	3592
Reflections used	7331	2782	2757
R_{int}	0.0212	0.0277	0.0249
R_1[a] [$I > 2\sigma$(i)]	0.0388	0.0346	0.0455
wR_2[b] [$I > 2\sigma(I)$]	0.1104	0.0967	0.1388

[a] $R_1 = \Sigma|F_0| - |F_c|/\Sigma|F_0|$. [b] $wR_2 = (\Sigma w||F_0| - |F_c||^2/\Sigma w|F_0|^2)^{1/2}$.

X-Ray structural determination

Single crystals of compound **3** suitable for X-ray crystallography were obtained by recrystallization from hexane. Single crystals of compound **14** were obtained by diffusing methanol into a toluene solution of the compound. Single crystals of compound **16** were obtained by diffusing THF into a benzonitrile solution of the compound. Data were collected on a Nonius Kappa CCD diffractometer using an Mo Kα (λ = 0.71073 Å) X-ray source and a graphite monochromator. Experimental details are described in Table 4. The crystal structures were solved using SIR 97[19] and SHELXL-97.[20] ORTEP drawings were made using ORTEP III for Windows.[21]

CCDC reference numbers 203273–203276. See http://www.rsc.org/suppdata/nj/b2/b211045h/ for crystallographic data in CIF or other electronic format.

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