Nuclear Magnetic Resonance Spectra of Organogermanium Compounds. Part 11.[1] Synthesis and Nuclear Magnetic Resonance Spectra of Tetramethyldigerma- and Octamethyltetragerma-cycloalkanes

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Digermamacrocycles ranging from 10- to 22-membered rings and tetragermamacrocycles ranging from 20- to 44-membered rings have been prepared and their ^{13}C and ^{73}Ge NMR spectra determined. A preliminary experiment indicates that the germamacrocycles possess no anion transfer properties.

In previous communications we have reported the preparation and structural study of 1-methyl-,[2] 1-phenyl-,[3] and 1-*tert*-butylgermacyclohexanes[4] and 1-methylgermacyclopentanes[1] based on ^{13}C and ^{73}Ge chemical shifts, molecular mechanics calculations (MM2) and molecular orbital calculations (MNDO).

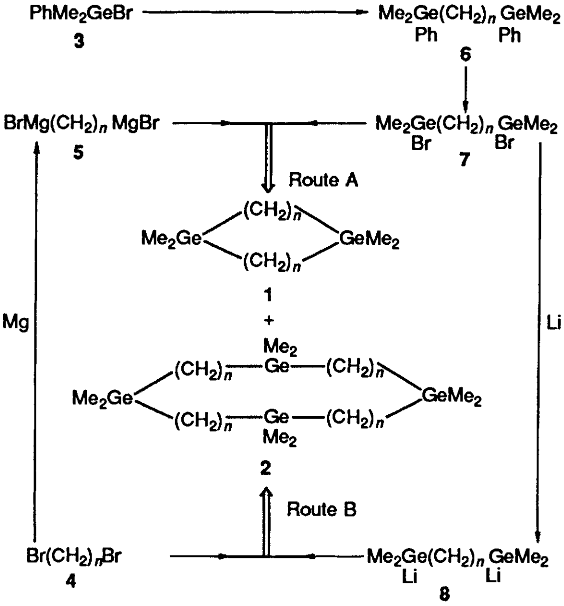
We decided to extend our work to germanium-containing large rings (germamacrocycles). The purpose of this investigation is twofold. Firstly, the preparation of germamacrocycles has not, to the best of our knowledge, been reported although there are some reports on the analogous silicon[5] and tin[6] compounds. Secondly, there is growing interest in the host–guest chemistry of complexation of a Lewis acidic host and an anion. The cryptand is an obvious example. Recently complexes of silicon-[5] or tin-containing[6] large rings and anions have been reported. In view of the slightly larger electronegativity of germanium relative to silicon or tin,[7] analogous germamacrocycles may be better hosts for anions. In this paper we describe the synthesis of a series of germamacrocycles and their NMR spectra. A preliminary result of the study of anion transport capability is also described.

Results and Discussion

Synthesis.—Generally speaking there are two possible routes to germamacrocycles when bromogermanes are used as the germanium source and α,ω-dibromoalkanes **4** as the carbon chain source. In view of the scarcity of commercially available organogermanium compounds, use of bromogermanes is the sole possibility. The coupling reaction of two components is expected to afford the 2:2 adduct **2** in addition to the main product, the 1:1 adducts **1**. The possibility of the formation of rings larger than **2** is very small if any, which turned out to be the case.

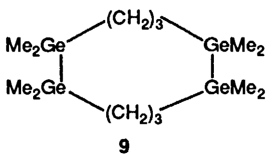
As is indicated in the Scheme, the first route (route A) is the coupling reaction between α,ω-dihalo-α,ω-digermaalkanes (**7**) and the bis-Grignard reagent of α,ω-dibromoalkanes (**5**). Route A has been successfully applied to the synthesis of **1b**–**1f** and **2b**–**2f**. Route A is the method of choice chiefly because of the ease of preparation of **5** as compared with that of **8** necessary for route B.

It was, however, difficult to prepare the bis-Grignard reagent (**5a**) of 1,3-dibromopropane (**4a**) under the reaction conditions.[8] Hence in an attempt to prepare the eight-membered **1a**, route B was taken. Route B is the reaction between α,ω-dilithio-α,ω-digermaalkanes (**8**) and α,ω-dibromoalkanes (**4**). When 1,5-dibromo-1,1,5,5-tetramethyl-1,5-digermapentane (**7a**) was treated with lithium followed by addition of 1,3-dibromopropane (**4a**), the expected **1a** was not obtained, but 1,1,2,2,6,6,7,7-octamethyl-1,2,6,7-tetragermacyclodecane (**9**) was isolated. The structure of **9** was confirmed by NMR spectra and elemental analysis. It is likely that a Wurtz-type reaction took place between **7a** and Li. Use of an excess of Li did not cause the formation of a Ge–Li bond. Presumably a bromolithio intermediate is formed, but an attempt to isolate the possible product, 1,1,2,2-tetramethyl-1,2-digermacyclopentane (**10**) was unsuccessful.



a; $n = 3$ **d**; $n = 6$
b; $n = 4$ **e**; $n = 8$
c; $n = 5$ **f**; $n = 10$

Scheme 1 Synthetic route to germamacrocycles



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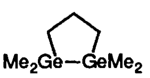

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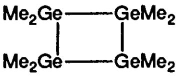

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Table 1 Boiling points, yields and analytical data for **6** and **7**

Compound (Formula)	Yield (%)	B.p./ °C (mmHg)[a]	Found (%) (required) C	 H
6a ($C_{19}H_{28}Ge_2$)	26	165 (5)	56.65 (56.82)	7.07 (7.03)
6b ($C_{20}H_{30}Ge_2$)	83	140 (0.1)	57.80 (57.82)	7.28 (7.28)
6c ($C_{21}H_{32}Ge_2$)	80	140 (0.1)	58.42 (58.70)	7.38 (7.51)
6d ($C_{22}H_{34}Ge_2$)	92	150 (0.1)	59.39 (59.56)	7.68 (7.72)
6e ($C_{24}H_{38}Ge_2$)	87	150 (0.1)	61.18 (61.11)	8.03 (8.11)
6f ($C_{26}H_{42}Ge_2$)	70	150 (0.1)	62.78 (67.48)	8.45 (8.47)
7a ($C_7H_{18}Ge_2Br_2$)	89	100 (0.1)	20.63 (20.65)	4.32 (4.46)
7b ($C_8H_{20}Ge_2Br_2$)	84	110 (0.1)	22.88 (22.82)	4.79 (4.69)
7c ($C_9H_{22}Ge_2Br_2$)	83	130 (0.1)	25.55 (24.84)	5.07 (5.09)
7d ($C_{10}H_{24}Ge_2Br_2$)	85	140 (0.1)	28.35 (26.73)	5.38 (5.38)
7e ($C_{12}H_{28}Ge_2Br_2$)	87	150 (0.1)	31.13 (30.19)	5.75 (5.91)
7f ($C_{14}H_{32}Ge_2Br_2$)	85	150 (0.1)	35.43 (33.27)	6.53 (6.53)

[a] The temperature of the Kugelrohr.

Table 2 Boiling (melting) points, yields and analytical data for **1**, **2** and **9**

Compound (Formula)	Yield (%)	B.p./°C (mmHg)[a] [M.p./°C]	Found (%) (required) C	 H
9 ($C_{14}H_{36}Ge_4$)	2	250 (0.1)	33.95 (34.01)	7.16 (7.34)
1b ($C_{12}H_{28}Ge_2$)	10	130 (0.1)	45.91 (45.42)	8.81 (8.89)
1c ($C_{14}H_{32}Ge_2$)	13	150 (0.1)	48.75 (48.63)	9.19 (9.34)
1d ($C_{16}H_{36}Ge_2$)	18	160 (0.1)	51.22 (51.46)	9.72 (9.72)
1e ($C_{20}H_{44}Ge_2$)	9	170 (0.1)	55.58 (55.92)	10.02 (10.32)
1f ($C_{24}H_{52}Ge_2$)	9	200 (0.1)	59.27 (59.35)	10.63 (10.79)
2b ($C_{24}H_{56}Ge_4$)	5	[63–65]	45.52 (45.42)	8.95 (8.89)
2c ($C_{28}H_{64}Ge_4$)	7	[63–65]	48.79 (48.63)	9.25 (9.34)
2d ($C_{32}H_{72}Ge_4$)	3	*b*	51.60 (51.46)	9.64 (9.64)
2e ($C_{40}H_{88}Ge_4$)	2	*b*	56.87 (55.92)	10.27 (10.32)
2f ($C_{48}H_{108}Ge_4$)	3	*b*	60.32 (59.35)	10.82 (10.79)

[a] The temperature of the Kugelrohr. [b] Melting points cannot be determined.

The preparation of 10-membered or larger rings was attempted *via* route A. This bis-Grignard reagent (**5b**) of 1,4-dibromobutane (**4b**) was treated with bromodimethylphenylgermane (**3**) to give 1,1,6,6-tetramethyl-1,6-diphenyl-1,6-digermahexane (**6b**). Bromination of **6b** afforded the necessary starting material, 1,6-dibromo-1,1,6,6-tetramethyl-1,6-digermahexane (**7b**). The other dibromo compounds **7c**–**7f** were prepared from **4c**–**4f** in a similar manner *via* **6c**–**6f**. The physicochemical and analytical data for **6b**–**6f** and **7b**–**7f** are given in Table 1.

Compound **7b** was caused to react with **5b** to afford a viscous liquid. The analysis, by means of high performance liquid chromatography, indicated that the liquid was a complex mixture. The desired 1,1,6,6-tetramethyl-1,6-digermacyclodecane (**1b**) was isolated in 10% yield by vacuum distillation and subsequent treatment of the distillate with medium pressure liquid chromatography. From the residue of the distillation 1,1,6,6,11,11,16,16-octamethyl-1,6,11,16-tetragermaicosane (**2b**) was isolated after chromatography over silica gel followed by repeated treatment with medium pressure liquid chromatography. The tetragermanium compound **2b** can be recrystallized from a mixture of hexane–diethyl ether (1:1).

It is interesting to note that formation of a small amount of octamethylcyclotetragermane (**11**) was indicated by mass (m/z = 414 and 298) and UV spectra (λ_{max} = 212 nm).[9] It is most likely that **11** was formed by a successive loss of the $-(CH_2)_4$-moiety from **2b** upon prolonged heating. This is in turn evidence of the formation of germamacrocycles.

The structure of **1b** and **2b** was further confirmed by a combination of elemental analysis, mass and NMR spectra. The symmetric nature of the structure is most clearly indicated by NMR spectroscopy, which will be described in the next section. As the final evidence, the structure of **1d** was determined by X-ray crystallographic analysis.[10] The ring has a C_i symmetry and [3434] conformation as is the case with cyclotetradecane.[11]

In a similar manner, digermacycles **1c**–**1f** and tetragermacycles **2c**–**2f** were obtained from the reaction between corresponding **7c**–**7f** and **5c**–**5f**, respectively. The larger the ring, the more difficult the separation and purification becomes. The yields, together with the results of elemental analyses of germamacrocycles **1** and **2**, are summarized in Table 2.

^{73}Ge *NMR Spectra.*—Because of its quadrupolar nature, the resonance of the ^{73}Ge nucleus tends to be broad, and this broadening is usually further enhanced as the molecular weight of the sample is increased. In this respect, it is rather surprising to find that all the germamacrocycles **1b**–**1f** and **2b**–**2f** gave ^{73}Ge signals. The width at half height is in the range of 35–130 Hz, which is reasonable in view of the other examples of unequally substituted tetraalkyl germanes.[12]

The chemical shifts are uniform, and there is a very small effect of the difference in the ring size. The shifts are in the range 1.2–6.2 and there is no direct correlation with the ring size. Since the shift of 1,1-dimethylgermacyclohexane (**12**) is -13.7[13] and that of 1,1-dimethyl-1-germacyclopent-3-ene is 39.8,[14] the effect of ring size upon chemical shift is large when the ring is small. In the case of germamacrocycles, the bond angles associated with germanium are essentially similar to that for tetramethylgermane ($\delta = 0$). This is in a good agreement with the structure determined by the X-ray analysis.[10]

The ^{73}Ge and ^{13}C chemical shifts of **1** and **2** together with the width at half height of the ^{73}Ge signals are summarized in Table 3.

^{13}C *NMR Spectra.*—^{13}C chemical shifts of germamacrocycles are also included in Table 3. For comparison and characterization, ^{13}C chemical shifts of compounds **6** and **7** are given in Table 4. The chemical shifts of Me, C-α and C-β for **6b** and **1b** are essentially identical to each other. Furthermore, the chemical shifts of Me and C-α are also equal to those of **12** [δ(Me) = -3.74; δ(C-α) = 15.3].[13] This is evidence for the partial structure $-CH_2CH_2GeMe_2CH_2CH_2-$ of **1** and **2**. Those of **7** are uniformly at lower field owing to the effect of bromine, and can be used for structural determination.

Mass Spectra.—The mass spectrum of **12** was previously analysed by us.[15] The spectrum gave a weak M^+ (m/z = 174) peak as well as the base peak at 89 (Ge$^+$Me). The most characteristic fragmentation pattern is loss of a methyl group ($m/z = M^+ - 15 = 159$) and subsequent loss of an ethylene moiety ($m/z = 131$). In order to obtain information on the fragmentation patterns of germamacrocycles, mass spectra of **1a** and **2a** were analysed.

For **1b**, a weak M$^+$ peak was observed at $m/z = 320$, and loss of a methyl moiety was also evident ($m/z = 305$). There was also evidence for the subsequent loss of an ethylene moiety ($m/z = 277$) and the second loss of the same moiety ($m/z = 249$). In view of the easy cleavage of C–Ge bonds in germacyclohexanes, it is expected that in digermacycles a simultaneous cleavage of two C–Ge bonds can lead to loss of a $-(CH_2)_4-$ moiety. For **1b**, the peaks at $m/z = 264$ and 208 are not strong at all, which indicates that the loss of $-(CH_2)_4-$ is not significant. For **2b**, there was no observed peak above $m/z = 200$. For the region below $m/z = 160$, the pattern is quite similar to that of **1b**.

Anion Migration Experiment.—A typical example of halide anion encapsulation is the equilibrium between halides and *in*,*in*-diazabicyclo[9.9.9]nonacosaneammonium ion.[16] In this particular case, the proton is directed toward the cavity, which makes the necessary ring size for encapsulation larger. On the other hand, encapsulation of halides by germamacrocycles will require a smaller ring size since there is no inner hydrogen.

With this in mind, we attempted the so-called U-tube test[17] for tetrabutylgermanes, **1b** and **1d**. Thus, in the bottom of a U-tube a dichloromethane solution of an organogermanium compound was placed and in the one end of the tube pure water was added while in the other end aqueous tetrabutylammonium halide was added. A small magnetic bar was placed in the organic solution which was stirred. A blank test was also performed where no germamacrocycles were placed in the organic layer.

The pure water was monitored at intervals with aqueous silver nitrate to detect the halide anion. No precipitate was observed after 10 h. Thus, it is evident that the germamacrocycles **1b** and **1d** have no anion-migrating property. It is likely that the Lewis acidity of the dimethylgermyl moiety is not strong enough to form a complex or an inclusion compound. Attempts are being continued in this laboratory to enhance the Lewis acidity of germamacrocycles so that an isolable complex can be prepared.

Table 3 ^{73}Ge[a] and ^{13}C[b] chemical shifts of germamacrocycles, **1** and **2** (in ppm)

Compound	Ge	Me	C-α	C-β	C-γ	C-δ	C-ε
1b	6.2 (67)[c]	−3.8	15.5	28.8			
1c		−3.9	15.3	24.7	36.8		
1d	5.0 (35)	−3.9	13.9	22.5	30.2		
1e	3.7 (45)	−3.8	14.9	24.5	28.0	32.5	
1f	1.9 (100)	−3.8	15.1	24.7	28.8	29.2	32.7
2b	5.0 (60)	−4.0	15.3	28.9			
2c	6.2 (100)	−4.0	15.5	24.8	37.0		
2d	1.9 (70)	−3.9	15.5	24.9	32.8		
2e	1.2 (130)	−3.9	15.5	25.1	29.1	33.2	
2f	5.0 (120)	−4.0	15.6	25.1	29.3	29.5	33.3

[a] Relative to external GeMe$_4$ ($\delta = 0$). [b] Relative to internal SiMe$_4$ ($\delta = 0$). [c] Values in parentheses are the half-width in Hz.

Experimental

Mass spectra were determined with a JEOL JMS-SX102. Liquid chromatography was carried out with the aid of Yamazen YFLC-540 with a 20 mm × 250 mm column packed with ODS 40.

The ^{73}Ge NMR spectra were recorded as solutions in CDCl$_3$ (1:1 v/v) on a JEOL FX-90Q spectrometer equipped with an NM-IT 10LF low-frequency insert, operating at 3.10 MHz, in a 10 mm tube at 30 °C. Typical measurement conditions were as follows: pulse width, 150 μs (90°): spectral width, 2000 Hz; number of scans, 5000; pulse delay, 100 ms; data points, 4096. The ^{13}C NMR spectra were determined for the same solutions on the same instrument at 22.50 MHz. Typical measurement conditions were as follows: pulse width, 13 μs (40°); spectral width, 2000 Hz; number of scans, 500; pulse delay, 1 s; data points, 4096.

Preparation of Germamacrocycles.—Tetrachlorogermane and α,ω-dibromoalkanes (**4**) were commercially available.

Bromodimethylphenylgermane (**3**). Tetrachlorogermane (0.056 mol) was treated with phenylmagnesium bromide prepared from an excess of bromobenzene (0.50 mol) to afford tetraphenylgermane (75%), m.p. 235–236 °C.[18] The bromination of tetraphenylgermane proceeds in a different manner depending on the amount of bromine used. Tetraphenyl germane (0.26 mol) was caused to react with excess bromine (0.56 mol) in boiling dibromoethane for 1 h. The usual work-up afforded dibromodiphenylgermane (95%), b.p. 140–145 °C at 0.1 mmHg.[19]

Dibromodiphenylgermane (0.01 mol) was treated with methylmagnesium iodide prepared from methyl iodide (0.01 mol) in diethyl ether and the mixture was refluxed for 3 h. The mixture was then hydrolysed with aqueous HCl and the organic layer was separated, dried and evaporated to give dimethyldiphenylgermane (92%), b.p. 180–190 °C at 15 mmHg.[20]

Dimethyldiphenylgermane (0.22 mol) in ethyl bromide (100 cm^3) was treated with bromine (0.22 mol) and the mixture was

Table 4 ^{13}C[a] chemical shifts of digermaalkanes, **6** and **7** (in ppm)

Compound	Me	C-α	C-β	C-γ	C-δ	C-ε	C-*ipso*	C-*o*	C-*m*	C-*p*
6a	−3.6	20.0	28.8				141.8	133.2	128.2	127.8
6b	−3.7	15.7	28.6				141.9	133.2	127.9	128.2
6c	−3.7	15.9	24.6	36.8			141.9	133.1	127.8	128.1
6d	−3.7	16.0	24.9	32.8			141.9	133.2	127.9	128.1
6e	−3.7	16.0	25.0	29.2	33.2		142.0	133.2	127.9	128.1
6f	−3.6	16.0	25.1	29.3[b]	29.6[b]	33.3	142.1	133.2	127.9	128.2
7a	4.2	19.8	24.8							
7b	3.9	21.3	26.8							
7c	4.0	21.9	23.9	34.9						
7d	4.0	22.0	24.1	31.7						
7e	4.1	22.1	24.3	28.9	32.2					
7f	4.0	22.1	24.3	29.1[b]	29.4[b]	32.3				

[a] Relative to internal SiMe$_4$ ($\delta = 0$). [b] Assignments may be exchanged.

refluxed for 1 h. The solvent and bromobenzene was removed and the residue was distilled with a Kugelrohr to give bromodimethylphenylgermane (**3**) (84%), b.p. 150 °C at 15 mmHg.[21]

α,α,ω,ω-Tetramethyl-α,ω-diphenyl-α,ω-digermaalkanes (**6b**–**6f**). The bis-Grignard reagent **5b** of 1,4-dibromobutane (**4b**) (0.01 mol) in diethyl ether (50 cm^3) was prepared, **3** (0.02 mol) in diethyl ether was added, and the ether was then removed. The residue was refluxed for 3 h, and hydrolysed with aqueous HCl. By evaporation of the organic layer 1,1,6,6-tetramethyl-1,6-diphenyl-1,6-digermahexane (**6b**) was obtained (85%), b.p. 140 °C at 0.1 mmHg. Other diphenyl compounds **6c**–**6f** were prepared from **3** and the corresponding **4c**–**4f** *via* the respective bis-Grignard reagents **5c**–**5f**.

α,ω-Dibromo-α,α,ω,ω-tetramethyl-α,ω-digermaalkanes (**7b**–**7f**). The digermyl compound **6b** (0.005 mol) was refluxed in ethyl bromide (30 cm^3) to which bromine (0.01 mol) was added and the reflux was continued for 1 h. Bromobenzene and the solvent were removed *in vacuo* and the residue was distilled by means of Kugelrohr to afford 1,6-dibromo-1,1,6,6-tetramethyl-1,6-digermahexane (**7b**) (86%), b.p. 110 °C at 0.1 mmHg. Other dibromo compounds **7c**–**7f** were prepared from the corresponding **6c**–**6f** and bromine in a similar manner.

Attempted preparation of **1a** *and* **1b**. To an ice-cooled mixture of $LiAlH_4$ (2.0 g, 0.05 mol) and diethyl ether (100 cm^3), bromodimethylphenylgermane (13 g, 0.05 mol) was slowly added and the mixture was stirred for 1 h at room temperature. After completion of the reaction, the mixture was hydrolysed, the ether layer dried, evaporated and the residue was distilled by Kugelrohr to afford dimethylphenylgermane (84%), b.p. 90 °C at 40 mmHg.[22] The Grignard reagent of allyl bromide (0.17 mol) was prepared from Mg (0.16 mol) in diethyl ether (100 cm^3) under ice cooling, to which, **3** (0.08 mol) in diethyl ether was added at room temperature and the mixture was stirred for 3 h. The mixture was hydrolysed by saturated aqueous ammonium chloride. The ether layer was separated, dried and the ether was removed. The residue was distilled by Kugelrohr to afford allydimethylphenylgermane (98%), b.p. 140 °C at 50 mmHg. The allyl compound (0.05 mol) and dimethylphenylgermane (0.05 mol) were heated at 200 °C for 10 h in the presence of azoisobutyronitrile (0.5 g). The mixture was distilled by Kugelrohr to give 1,1,5,5-tetramethyl-1,5-diphenyl-1,5-digermapentane (**6a**) (26%), b.p. 165 °C. **6a** (10 g, 0.025 mol) was treated with bromine in the same manner as **6b**–**6f** to afford the 1,5-dibromo-1,1,5,5-tetramethyl-1,5-digermapentane **7a** (9 g; 89%), b.p. 110 °C at 0.1 mmHg. Li (0.2 g, 0.029 mol) and hexamethylphosphortriamide (HMPA) (10 g, 0.056 mol) were dissolved in THF (30 cm^3), to which **7a** (5 g, 0.012 mol) in THF (30 cm^3) was added to prepare **8a**. After stirring for 3 h at room temperature, THF was added to make the volume of the solution up to 100 cm^3. A THF (380 cm^3) solution of **4a** (2.5 g, 0.012 mol) was prepared, to which the solution containing **8a** was added at 0 °C, and the mixture was stirred for 2 days at room temperature. The mixture was washed with water, dried and evaporated to give a viscous liquid. By repeated purification with the aid of liquid chromatography, 1,1,2,2,6,6,7,7-octamethyl-1,2,6,7-tetragermacyclodecane (**11**) was isolated in 2% yield.

Germamacrocycles **1** *and* **2**. The bis-Grignard reagent **5b** of 1,4-dibromobutane (0.01 mol) in diethyl ether (100 cm^3) was prepared as described above. The mixture of 1,6-dibromo-1,1,6,6-tetramethyl-1,6-digermahexane (**7b**) (0.01 mol) and diethyl ether (200 cm^3) was stirred under ice-water, to which the bis-Grignard reagent was slowly added. The mixture was stirred for 2 days at room temperature. After treatment of the mixture with aqueous HCl (2 mol dm^{-3}), the ether layer was separated, dried and the ether was removed. The residue was distilled by Kugelrohr to give a viscous residue, which was chromatographed on silica gel to remove the starting material and polymeric by-products.

From the crude product, 1,1,6,6-tetramethyl-1,6-digermacyclodecane (**1b**) and 1,1,6,6,11,11,16,16-octamethyl-1,6,11,16-tetragermaicosane (**2b**) were isolated by successive application of reverse phase medium pressure liquid chromatography. The preparation of other germamacrocycles **1c**–**1f** and **2c**–**2f** were carried out in an essentially identical manner.

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