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Synthesis of 5,5,6,6,21,21,22,22-octamethyl-5,6,21,22-tetragerma[10.10]paracyclophane

Yoshito Takeuchi *, Yoshitake Suzuki, Fumiyasu Ono, Kenji Manabe

Department of Chemistry, Faculty of Science, Kanagawa University, 2946 Tsuchiya, Hiratsuka-shi 259-1293, Japan

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Abstract

A [10,10]paracyclophane, 5,5,6,6,21,21,22,22-octamethyl-5,6,21,22-tetragerma[10.10]paracyclophane (**4a**), with two $-R^1R^2GeGeR^1R^2-$ moieties in the center of two bridges, was prepared. An attempt to synthesize cyclophanes, **4b** ($R^1 = Me$; $R^2 = Ph$) and **4c** ($R^1 = R^2 = Ph$) was also made. The products were not analytically pure even after strenuous purification procedure to indicate that a double Wurtz coupling reaction is extremely difficult and necessarily accompanied by formation of polymeric by-products.

Keywords: Wurtz coupling; Cyclophanes; Organogermanium compound; ditopic host

1. Introduction

Cyclophanes are one of the most interesting classes of organic compounds from a structural point of view. Since the first report of this class of compounds [1], a large number of analogous compounds have been reported [2]. One interesting aspect of cyclophanes is their ability to act as hosts of a variety of chemical species [3].

Attempts have been made to improve the selectivity or the ability of cyclophanes to act as hosts by introducing side chains on the aromatic ring containing heteroatoms. Further attempts have been made to modify cyclophanes by introducing side chains of the aromatic ring containing heteroatoms [4]. Attempts have also been made to introduce heteroatoms into appropriate positions on the bridge [5].

As a part of our extensive study of novel hosts containing germanium [6], we were interested in cyclophanes modified with a germanium-containing moiety. The first germanium-containing cyclophane, 1,1,2,2,9,9,10,10-octamethyl-1,2,9,10-tetragerma[2.2]paracyclophane (**1**), was reported by Sekiguchi et al. [7]. This compound has a variety of interesting feature: firstly, the synthesis itself is a challenge since a Ge–Ge bond is weaker than the corresponding C–C bond, secondly, a comparison of structural parameters such as bond lengths and bond angles with those of silicon- and carbon-analogues, 1,1,2,2,9,9,10,10-octamethyl-1,2,9,10-tetrasila[2.2]paracyclophane (**2**), and 1,1,2,2,9,9,10,10-octamethyl[2.2]paracyclophane (**3**), and thirdly a similar comparison of the extent of π–π interaction between two parallel aromatic rings in these cyclophanes [8].

We believed that enlarging the cavity of **1**, which consisted of two aromatic rings and two bridges made of two germanium atoms, would allow the cavity to act as a kind of heteroditopic host, i.e. a host which can interact both a cationic and an anionic guest. Thus, this molecule could capture and/or transport zwitterionic species such as amino acids.

It had previously been established that germanium-containing large rings can capture and transport halide ions [9]. A possible cation-π interaction [10] between the positive side of the guest and the aromatic rings allowed the cyclophane with an enlarged cavity to act as a heteroditopic host.

With this in mind, we attempted to synthesize a germacyclophane with a much larger cavity, viz.

* Corresponding author. Tel: +81-463-59-4111; fax: +81-463-58-9684.
E-mail address: yoshito@chem.kanagawa-u.ac.jp (Y. Takeuchi).

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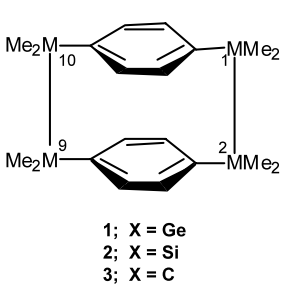
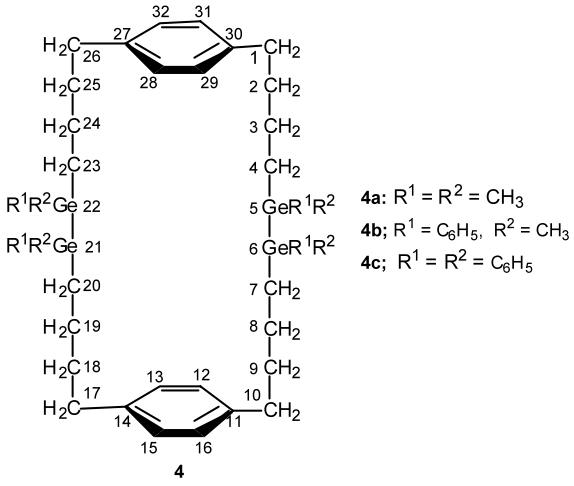
5,5,6,6,21,21,22,22-octamethyl-5,6,21,22-tetragerma[10.10]paracyclophane (**4a**). Preliminary MM2 calculations indicated that the size of the cavity of **2** was ca. 9A (e.g. C11–C30 = 9.220 A) by ca. 12 A (e.g. Ge5–Ge22 = 12.011 A), which was large enough to accommodate small amino acids.





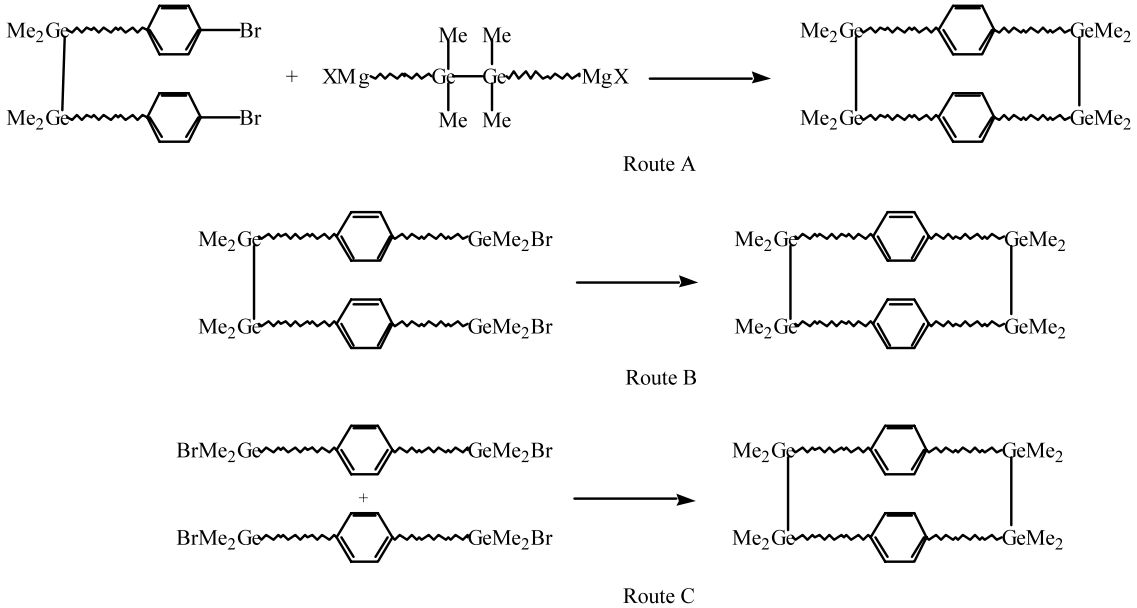
2. Results and discussion

2.1. Strategy of synthesis

Several methods are possible for the synthesis of macrocyclic organogermanium compounds as are depicted in Scheme 1.

Route A is a ring closure by a Grignard reaction which is probably the most frequently used pathway. Thus, Sakurai et al. [11] synthesized the first cyclophane, **2**, which has a bridge made of silicon, although in low yield (1.6%). Routes B and C are intra- and intermolecular Wurtz coupling reactions, respectively. Routes A and B involve a digermane with a relatively weak Ge–Ge bond and thus there is always some danger of a Ge–Ge bond cleavage during the final ring closure [12]. Furthermore, the intermediate digermane is difficult to synthesize.

Regarding route C, intermolecular cyclizations of this type have an apparent statistical disadvantage since the



Scheme 1. Possible synthetic procedure of tetragerma-macrocycles.

intermolecular coupling necessarily competes with the intramolecular cyclization. On the other hand, route C has an advantage in that the weaker Ge–Ge bond is formed at the final stage of the reaction and that the synthesis of the precursor is relatively easy. Taking these factors into consideration, we decided to employ the route C for our attempt to synthesize **4a**.

The necessary precursor of **4a**, 1,4-bis(4-(bromodimethylgermyl)butyl)benzene (**5a**) was prepared as shown in Scheme 2. It was thought that hydrogermylation of 1,4-bis-(3-butenyl)benzene, (**8**), with dimethylphenylgermane (**7a**) is the method of choice to prepare **5a**.

We prepared **8** in 64% yield by a coupling reaction between 3-bromopropene and 1,4-bis(chloromethyl)-benzene, (**9**), in the presence of Mg. Linder et al. [13] also prepared **8** from 1,4-bis(bromomethyl)benzene in 63% yield. Since the yields are comparable, the synthesis described in this paper may be regarded as superior, as the chloride precursor is considerably cheaper than the bromide. It is noteworthy, however, that the ^{1}H-NMR data reported by Linder et al. was different from the data presented in this paper. There is no ambiguity in the assignment of ^{1}H-NMR data presented in this paper, since it is based on H–H and H–C COSY experiments.

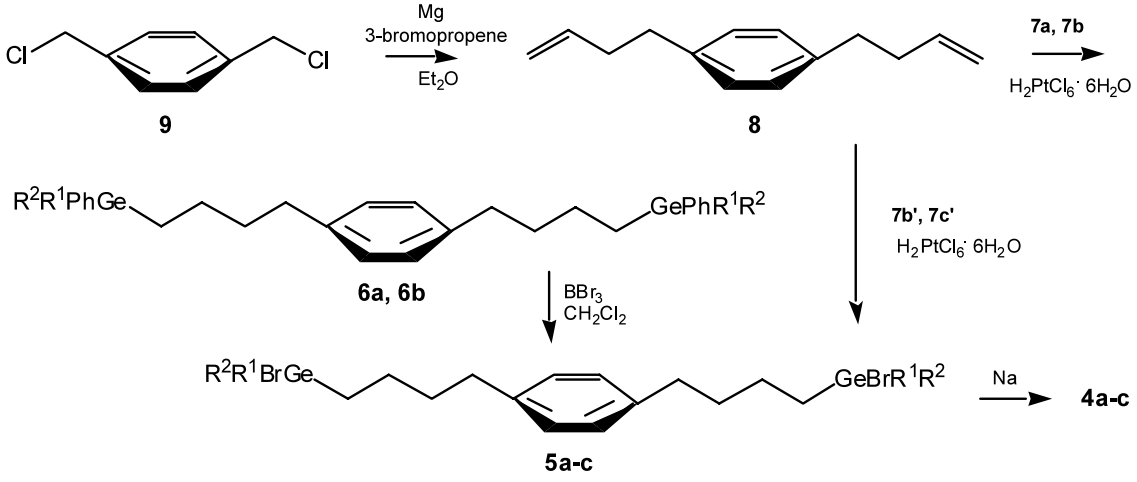
The germanium compound dimethylphenylgermane **7a** was prepared from tetrachlorogermane via tetraphenylgermane, dibromodiphenylgermane, dimethyldiphenylgermane, bromodimethylphenylgermane and dimethylphenylgermane, other germanium compounds were prepared in a similar manner.

Hydrogermylation of **8** with **7a** gave 1,4-bis(4-(dimethylphenylgermyl)butyl)benzene (**6a**) in 49% yield. It is a standard method of organogermanium chemistry to use bromine to prepare bromogermane from phenylgermane [14]. This method is not, however, always applicable particularly when the compound contain a benzyl (or $ArCH_2^-$) moiety that is susceptible to the Ge–benzyl bond cleavage by bromine. Recently, it was found that boron tribromide, BBr_3, is an excellent reagent for affecting phenyl–bromine exchange without cleavage of the Ge–benzyl bond [15]. The phenyl–bromine exchange with BBr_3 took place smoothly to convert **6a** into **5a** in 39.5% yield while bromination with Br_2 resulted in poor yield.

In the final stage of the synthesis, a double Wurtz coupling of **5a** was attempted under various conditions. The best result was obtained when the reaction was carried out in toluene with Na in the presence of a catalytic amount of tetraphenylethylene (TPE) [16]. After a series of strenuous purification procedures, a small amount of 5,5,6,6,21,21,22,22-octamethyl-5,6,21,22-tetragerma[10.10]paracyclophane (**4a**) was obtained as a colorless oil. The yield of **4a** was as low as 0.86%, which was not unexpected for a double Wurtz coupling reaction. A large amount of uncharacterisable polymeric materials was also obtained. Sakurai et al. [11] reported that the yield of the cyclic product by the Wurtz coupling reaction was improved in the presence of 18-crown-6. The Wurtz reaction was attempted in this manner, but **4a** was not obtained.

2.2. Characterization of *4a*

The most persuasive evidence for the formation of **4a** was given by EI-MS measurements. The expected molecular ion peak was observed in the EI-MS spectrum at *m/e* 786, and, furthermore, peaks around the



a: $R^1 = R^2 = CH_3$
b; $R^1 = C_6H_5$, $R^2 = CH_3$
c; $R^1 = R^2 = C_6H_5$

Scheme 2. Synthesis of **4**.

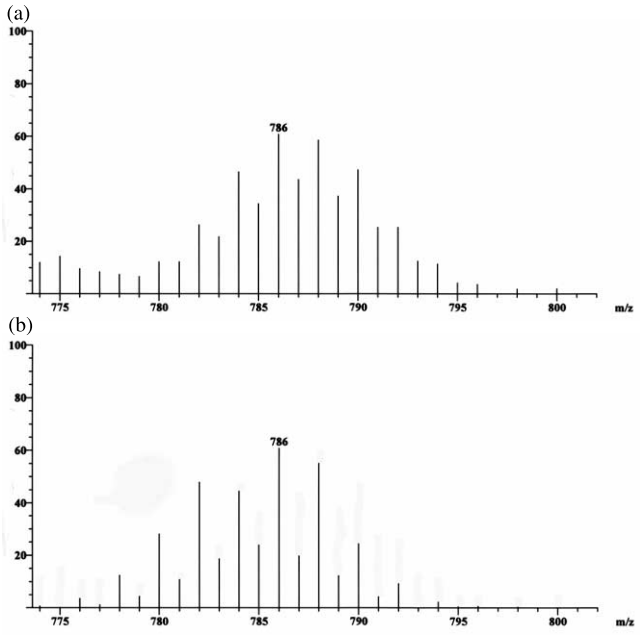


Fig. 1. Characteristic mass spectral pattern of compounds containing four germanium atoms.

molecular ion peak form a characteristic pattern that is associated with a species containing four germanium atoms. Fig. 1 shows the observed pattern (a) and calculated pattern for species containing four germanium atoms (b). The agreement between (a) and (b) is reasonable, indicating that **4a** does contain four germanium atoms.

Other evidence for the structure of **4a** included the ^{1}H- and ^{13}C-NMR spectra of **8**, **9**, **6a**, **5a** and **4a**. The relevant NMR data are given in Tables 1 and 2. For ease of comparison the numbering of **8**, **9**, **6a** and **5a** for NMR data follows that of **4a**.

The connectivity was established by means of H–H and H–C COSY experiments. It is evident that the –C–C–C–C– moiety is present in all these compounds.

2.3. Attempts to synthesize other germacyclophanes

Based on the MS and NMR spectral data, it was confirmed that the Wurtz coupling of dibromogermane, **5a**, gave the desired cyclic tetragermane **4a** in low yield. However, experimental evidence [17] suggested that organogermanium hosts show poor ability to capture and transport anions unless the alkyl substituent on the germanium atom is replaced by the halogen.

With this in mind, we attempted to prepare 5,6,21,22-tetramethyl-5,6,21,22-tetraphenyl-5,6,21,22-tetragerma[10.10]paracyclophane (**4b**) and 5,5,6,6,21,21,22,22-octaphenyl-5,6,21,22-tetragerma[10.10]paracyclophane

Table 1
^{1}H-NMR spectral data of **8**, **6a**, **6b**, **5a**, **5b**, **5c**, **4a** and **4b** in $CDCl_3$

	8 [a]			
H_1	2.68 (t, $^{vic}J = 7.8$ Hz)			
H_2	2.39–2.33 (m)			
H_3	5.86 ($^{trans}J = 17.1$ Hz; $^{cis}J = 10.3$ Hz; $^{vic}J = 0.0$ Hz)			
H_4	4.97*cis* ($^{cis}J = 10.3$ Hz; $^{gem}J = 1.8$ Hz; $^{allyl}J = 1.7$ Hz)			
	5.04*trans* ($^{trans}J = 17.1$ Hz; $^{gem}J = 1.8$ Hz; $^{allyl}J = 1.7$ Hz)			
H_{31}	7.11			
GeMe	–			
	8 [b]	**6a** [c]	**6b**	**5a**
H_1	2.95 (t, $^{vic}J = 7.8$ Hz)	2.54 (t, $^{vic}J = 7.8$ Hz)	2.53 (t, $^{vic}J = 7.8$ Hz)	2.60 (t, $^{vic}J = 7.8$ Hz)
H_2	2.68–2.60 (m)	1.64–1.58 (m)	1.66–1.60 (m)	1.70–1.64 (m)
H_3	6.22–6.08 (m)	1.48–1.41 (m)	1.54–1.48 (m)	1.59–1.53 (m)
H_4	5.36–5.24	0.99–0.96	1.29–1.25	1.22–1.19
H_{31}	7.38	7.03	6.99	7.08
GeMe	–	0.35	0.61	0.67
GePh		7.46–7.32	7.46–7.31	–
	5b	**5c**	**4a**	**4b**
H_1	2.58 (t, $^{vic}J = 7.8$ Hz)	2.56	2.53 (t, $^{vic}J = 7.6$ Hz)	2.52 (t)
H_2	1.70–1.58 (m)	1.80–1.63 (m)	1.59–1.53 (m)	1.62–1.53 (m)
H_3	1.70–1.58 (m)	1.80–1.63 (m)	1.37–1.30 (m)	1.45–1.34 (m)
H_4	1.53–1.50	1.80–1.63	0.81–0.78	1.20–0.99
H_{31}	7.04	7.00	7.05	7.05
GeMe	1.00	–	0.13	0.39
GePh	7.58–7.40	7.59–7.33	–	7.27–7.23

[a] This study.
[b] Ref. [13].
[c] Aromatic ring bonded to germanium; 7.46–7.32 (m, 10H).

Table 2
^{13}C-NMR spectral data of **8**, **6a**, **6b**, **5a**, **5b**, **5c**, **4a** and **4b** in $CDCl_3$

No.	**8** [a]	**8** [b]	**6a**	**6b**	**5a**	**5b**	**5c**	**4a**	**4b**
C_1	35.0	35.6	35.2	35.0	35.0	34.9	35.0	35.0	34.8
C_2	35.5	36.2	35.1	35.0	34.3	34.2	34.3	34.8	34.7
C_3	138.2	138.7	24.8	24.7	23.6	24.1	24.3	25.5	25.4
C_4	114.8	114.8	15.9	14.5	21.5	20.7	19.4	16.4	15.7
C_{30}	139.3	139.8	139.8	139.5	139.6	137.7	135.6	139.7	139.7
C_{31}	128.3	129.3	128.1	128.2	128.3	128.4	128.4	128.3	127.9
GeMe	–	–	−3.6	−5.2	3.4	2.2	–	−3.8	−5.0
GePh			127.8	128.0		128.3	128.1		127.8
			128.1	128.5		130.0	130.1		128.3
			133.1	133.9		132.7	133.5		133.8
			141.8	139.8		139.6	139.4		141.1

[a] This study.
[b] Ref. [13].

(**4c**), since both **4b** and **4c** may be converted to the corresponding bromide by a phenyl–bromine exchange reaction with BBr_3.

In principle **4b** and **4c** could be prepared in a similar manner as the preparation of **4a**, as shown in Scheme 2, if appropriate precursors **5b** and **5c** were synthesized.

5b was prepared by two methods. The first method, (method A), was the bromination of 1,4-bis(4-(methyldiphenylgermyl)butyl)benzene (**6b**). **6b** was obtained by the hydrogermylation of **8** with methyldiphenylgermane (**7b**). The other method, (method B), was the hydrogermination of **8** with bromomethylphenylgermane (**7b′**) (Scheme 2).

A Wurtz coupling reaction of **5b** afforded a small amount of **4b**, as was verified by ^{1}H- and ^{13}C-NMR spectroscopy. Because of the inevitable contamination by various by-products, an analytically pure sample of **4b** was not obtained. It is interesting to notice that the obtained sample was a mixture of stereoisomers as was indicated by the NMR spectra.

The precursor **5c** was prepared via the hydrogermylation of **8** with bromodiphenylgermane (**7c′**). A Wurtz coupling reaction of **5c** also afforded a small amount of **4c**, as was verified by ^{1}H- and ^{13}C-NMR spectroscopy. Here again, due to the contamination by various by-products, separation of an analytically pure sample of **4c** was unsuccessful. Preparations of the necessary organogermanium species **7b**, **7b′** and **7c′** are carried out by the methods described in the literature.

These results indicated that the synthesis of pure cyclophanes with germanium atom(s) in the bridge was extremely difficult, and was impractical as a method of synthesizing more than trace amounts of the respective host molecule. It appeared that the synthesis of cyclophanes with side arms containing a germanium moiety on the aromatic ring would be more feasible. Further study along these lines is in progress in our laboratory.

3. Experimental

^{1}H-NMR spectra were determined on a JEOL EX-400 spectrometer operating at 400 MHz, and the chemical shifts were reported in δ (ppm) with respect to Me_4Si. ^{13}C-NMR spectra were determined on a JEOL EX-400 spectrometer operating at 100 MHz and the chemical shifts were reported in δ (ppm) with respect to Me_4Si. Mass spectra were recorded on JEOL NS-MP09 mass spectrometer operating in the EI mode at 70 eV or on a PerSeptive Biosytemes DE MALDI-TOF mass spectrometer, Voyager Elite XL. Elemental analysis was carried out with a Perkin–Elmer Series II CHNS/O Elemental Analyzer or by the Microanalytical Laboratory, Department of Chemistry, The Graduate School of Science, The University of Tokyo.

3.1. 1,4-Bis(3-butenyl)benzene (8)

To a solution of 2.4 g (0.1 mol) of magnesium turnings in Et_2O (75 ml) was added dropwise 12.2 g (0.1 mol) of 3-bromopropene in Et_2O (75 ml). The mixture was refluxed for 1 h at room temperature. A solution containing 5.2 g (0.03 mol) of 1,4-bis(chloromethyl)benzene (**9**) in THF (50 ml) was added and the mixture was refluxed for 2 h, which was hydrolyzed by water (15 ml) and aq. NH_4Cl (25 ml). The ether layer was separated, dried and the solvent was evaporated. The crude product was distilled under reduced pressure (9 mmHg, 110 °C) to yield a colorless liquid of **8** (3.5 g, 0.02 mol, 64%).

The preparations of **7a** [17], **7b** [17] and **7c′** [18] were previously described in the literature.

3.2. Bromomethylphenylgermane (7b′)

A mixture of methylphenylgermane [18] (1.07 g, 6.4 mmol) and NBS (1.14 g, 6.4 mmol) in hexane (16 ml)

was refluxed for 4 h. The solvent was evaporated after the remaining NBS was filtered off. The crude product was distilled under reduced pressure (20 mmHg, 130 °C) to yield a colorless liquid of **7b′** (1.02 g, 4.2 mmol, 65%). Anal. Calc. for C_7H_9GeBr: C, 34.22; H, 3.69. Found: C, 34.43; H, 3.69. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.16 (3H, d, $J = 2.3$ Hz, Ge–CH_3), 5.85 (m, 1H, Ge–H), 7.42–7.62 (m, 5H, Ge–Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 1.8 (Ge–CH_3), 128.6, 130.5, 133.0, 135.4 (Ge–Ph).

3.3. 1,4-Bis(4-(dimethylphenylgermyl)butyl)benzene (**6a**)

A mixture of **7a** (2.63 g, 15 mmol) and **8** (1.25 g, 6.45 mmol) was stirred at 100 °C for 1 h. The mixture was further stirred for 7 h after the catalytic amount of $H_2PtCl_6 \cdot 6H_2O$ was added. The mixture was extracted by Et_2O and the solvent was evaporated. The crude product was distilled under reduced pressure (9 mmHg, 120 °C) to remove volatile material. The resulting solution was purified by GPC with $CHCl_3$ to yield a colorless oil of **6a** (1.40 g, 2.6 mmol, 40%). Anal. Calc. for $C_{30}H_{42}Ge_2$: C, 65.77; H, 7.73. Found: C, 65.64; H, 7.74.

3.4. 1,4-Bis(4-(bromodimethylgermyl)butyl)benzene (**5a**)

To a solution of **6a** (5.87 g, 11 mmol) in 65 ml of CH_2Cl_2 was added dropwise boron tribromide (21 ml (1 M in CH_2Cl_2), 21 mmol). The mixture was stirred for 1 h below 0 °C and additional 6 h at room temperature. The remaining boron tribromide was inactivated by 20 ml of water and the mixture was extracted by CH_2Cl_2. The solvent was evaporated and the residue was purified by GPC with $CHCl_3$ to yield a pale yellow oil of **5a** (2.54 g, 4.6 mmol, 42%), DE MALDI-TOFMS; *m/z*: 574.23, 576.22, 577.23, 578.23, 579.24, 580.24, 581.23, 582.23, 583.22, 584.22. ($C_{18}H_{32}Ge_2Br_2$, 576.92).

3.5. 5,5,6,6,21,21,22,22-octamethyl-5,6,21,22-tetragerma[10.10]Paracyclophane (**4a**)

A mixture of Na (3.17 g; 140 mmol) and toluene (190 ml) was refluxed for 3 h in the atmosphere of argon. The mixture was cooled to room temperature, to which TPE (0.229 g; 0.69 mmol) was added and stirred for 2 h. A toluene solution (100 ml) of **5** (3.77 g; 6.8 mmol) was added dropwise in 19 h with stirring. The stirring was continued for 276 h at room temperature. The remaining Na was filtered off, and the polymeric by-produces was removed by means of column chromatography (silica gel; CH_2Cl_2:$Et_2O = 1:1$). The eluate was evaporated and the remaining material was purified by means of GPC to afford colorless liquid of **4a** (46 mg, 0.058 mmol, 0.86%). EIMS; *m/z*: 786 ([M^+]: $C_{36}H_{64}^{70}Ge^{72}Ge^{74}Ge_2$, 786.19).

3.6. 1,4-Bis(4-(methyldiphenylgermyl)butyl)benzene (**6b**)

A mixture of **8** (1.86 g, 10 mmol) and methyldiphenylgermane (**7b**) (5.34 g, 20 mmol) was stirred at 100 °C for 1 h. The mixture was further stirred for 7 h after the catalytic amount of $H_2PtCl_6 \cdot 6H_2O$ was added. The mixture was extracted by Et_2O and the solvent was evaporated. The crude product was distilled under reduced pressure to remove volatile material. The resulting solution was purified by means of column chromatography (silica gel, $CHCl_3$) to yield a pale yellow oil of *1,4-bis(4-(methyldiphenylgermyl)butyl)benzene* (**6b**) (4.70 g, 7.0 mmol, 70%). Anal. Calc. for $C_{40}H_{46}Ge_2$: C, 71.49; H, 6.90. Found: C, 71.20; H, 6.80.

3.7. 1,4-Bis(4-(bromomethylphenylgermyl)butyl)benzene(**5b**)

3.7.1. Method A

To a refluxing solution of **6b** (4.7 g, 7.0 mmol) in CCl_4 (50 ml) was added dropwise Br_2 (3.2 g, 20 mmol) in CCl_4 (10 ml) in 2 h with refluxing and stirring, which was continued for 5 h. The solvent was evaporated and the residue was purified by GPC with $CHCl_3$ to yield a pale brown oil of **5b** (0.52 g, 0.8 mmol, 11%). Anal. Calc. for $C_{28}H_{36}Br_2Ge_2$: C, 49.63; H, 5.35. Found: C, 49.45; H, 5.21.

3.7.2. Method B

A mixture of **8** (1.86 g, 10.0 mmol) and **7b** (5.89 g, 24.0 mmol) was stirred at 100 °C for 1 h. The mixture was further stirred for 11 h after the catalytic amount of $H_2PtCl_6 \cdot 6H_2O$ was added. The mixture was extracted by Et_2O and the solvent was evaporated. The crude product was distilled under reduced pressure to remove volatile material. The resulting solution was purified by GPC with $CHCl_3$ to yield a colorless oil of **5b** (2.73 g, 4.0 mmol, 63%).

3.8. Attempted preparation of 5,6,21,22-tetramethyl-5,6,21,22-tetraphenyl-5,6,21,22-tetragerma[10.10]paracyclophane (**4b**)

(a) In THF: A mixture of Na (1.20 g, 50 mmol) and TPE (0.1 g, 0.3 mmol) in THF (80 ml) was stirred for 1 h at room temperature in the atmosphere of nitrogen. A THF solution (40 ml) of precursor **5b** (2.16 g; 2.08 mmol) was added dropwise in 19 h with stirring. The stirring was continued for 67 h at room temperature. The remaining Na was filtered off, and the polymeric by-produces were removed by means of column chro-

matography (silica gel, hexane–CH_2Cl_2–Et_2O = 4:1:0–0:1:1). The eluate was evaporated and the remaining material was purified by means of GPC to afford colorless liquid of **4b** (10 mg, 0.01 mmol) in 0.46% yield.

(b) In toluene: The reaction was carried out in toluene. The result was much the same with the reaction in THF. The yield of **4b** was 10 mg (0.46%).

3.9. 1,4-Bis(4-(bromodiphenylgermyl)butyl)benzene (5c)

A mixture of **8** (2.42 g, 13.0 mmol) and bromodiphenylgermane (**7c′**) (12.0 g, 19.5 mmol) was stirred at 80 °C for 30 min. The mixture was further stirred for 10 h after the catalytic amount of $H_2PtCl_6 \cdot 6H_2O$ was added. The mixture was extracted by benzene and the solvent was evaporated. The crude product was distilled under reduced pressure (9 mmHg, 180 °C) to remove volatile material. The resulting solution was purified by GPC with $CHCl_3$ to yield a colorless oil of **5c** (7.20 g, 9.0 mmol, 69%).

3.10. Attempted preparation of 5,5,6,6,21,21,22,22-octaphenyl-5,6,21,22-tetragerma[10.10]paracyclophane (4c)

A mixture of Na (2.32 g, 60 mmol) and TPE (0.10 g, 0.3 mmol) in toluene (80 ml) was stirred for 1 h at room temperature in the atmosphere of nitrogen. A toluene solution (45 ml) of precursor **5c** (1.61 g; 2.09 mmol) was added dropwise in 19 h with stirring. The stirring was continued for 240 h at room temperature. The remaining Na was filtered off, and the polymeric by-products were removed by means of column chromatography (silica gel, CH_2Cl_2–Et_2O = 1:1). The eluate was evaporated and the remaining material was attempted to purify by means of GPC, but pure **4c** was not obtained because many by-products were present.

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