1,8-Dimethyl-1,8-dihalo-1,8-digermacyclotetradecanes. The First Germamacrocycles with Anion Transport Capability

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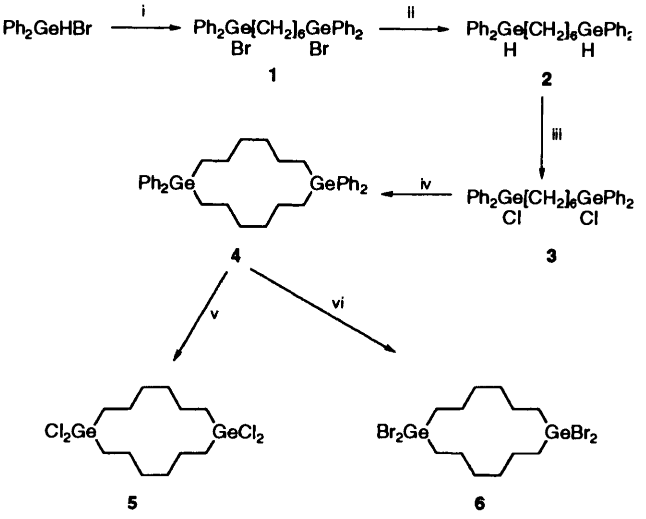
It has been shown that 1,8-dichloro-1,8-dimethyl-1,8-digermacyclotetradecane transports chloride anion more effectively than bromide anion in a U-tube test. The dibromo analogue also can transport anions. The efficiency of transport of open chain analogues with a similar environment around germanium is inferior to that of cyclic systems which confirms the essential role of the ring structure for anion transport. The anion transport capability was examined for other germanium-containing 14-membered rings. A possible mechanism for anion transport is proposed.

In a previous communication, we have reported the preparation of a variety of di- and tetra-germamacrocycles ranging from 10-membered to 44-membered rings.[1] We expected that some of these germamacrocycles might possess the anion transport capability in analogy with the corresponding silicon-[2] and tin-[3]containing large rings. It was found out, however, that all of methyl-substituted germamacrocycles we have prepared failed to show any of this capability.

The size of the cavity of a 14-membered 1,1,8,8-tetramethyl-1,8-digermacyclotetradecane **7** is not large, and the distance between the inner hydrogen of C-2 and that of C-10 can be as short as 2.3 Å,[4] which is not enough to hold an anion. On the other hand, if the Lewis acidic character of the germanium moiety is large enough, either nesting complexation or apolar surface interactions might be in action[2] though cavity inclusion complexation is impossible.

It was expected that replacement of one or two of the methyl groups with electron-withdrawing substituents such as halogens would increase the Lewis acidity of the germanium moiety. It was also thought interesting to estimate the effect of a hydrogen or a phenyl group on germanium on the Lewis acid character of the germanium moieties. In this paper we describe the synthesis of halo or phenyl substituted 1,8-digermacyclotetradecanes and their anion transport capability.



Scheme 1 Synthetic route to 1,1,8,8-tetrahalo-1,8-digermacyclotetradecanes **5**, **6**. *Reagents and conditions:* i, hexa-1,5-diene–hexane, reflux, 5 h; ii, LAH–Et$_2$O, reflux, 3 h; iii, CCl$_4$, reflux, 5 h; iv, (*a*) Li–THF, (*b*) Br(CH$_2$)$_6$Br–THF; v, HCl–AlCl$_3$, PhH, room temp.; vi, Br$_2$–1,2-dibromoethane.

Results and Discussion

Synthesis.—In an attempt to introduce halogens on germanium, we first thought that the reaction of 1,6-bis(trichlorogermyl)hexane or 1,6-bis(tribromogermyl)hexane with the Grignard reagent of 1,6-dibromohexane would afford the desired 1,1,8,8-tetrachloro-1,8-digermacyclotetradecane **5** or 1,1,8,8-tetrabromo-1,8-digermacyclotetradecane **6** in a straightforward manner. The attempted reaction gave, however, an intractable mixture, which indicates that selective reaction with one halogen out of three is difficult. Hence we searched for the other approaches.

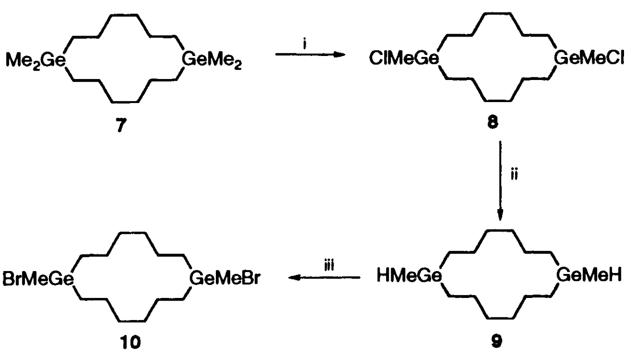
Since the reaction of bromine (Br$_2$) on phenylgermyl derivatives gives bromogermyl derivatives in a moderate yield,[5] it was expected that 1,1,8,8-tetraphenyl-1,8-digermacyclotetradecane **4** would be a good precursor for **5** or **6**. It was expected at first that the reaction of dibromo- (or dichloro-) diphenylgermane with the bis-Grignard reagent of 1,6-dibromohexane would, as was the case with the preparation of **7**,[1] easily afford **4**. To our disappointment, this reaction also gave an intractable mixture of a polymeric product. Hence we decided to take an alternative approach where the polarity of the germanium was reversed from cationic to anionic. Thus, **4** was prepared *via* a bisgermyllithium derivative as indicated in Scheme 1.

As described later, however, both **5** and **6** were gradually hydrolysed upon contact with H$_2$O, *i.e.*, during the estimation of anion-transport capability. To retard the hydrolysis, one of the halogens in the geminal dihalogermyl moieties of **5** and **6** was replaced by a methyl group. Hence, we attempted to prepare derivatives with halo(methyl)germyl moieties. The procedure for the preparation of 1,8-dichloro-1,8-dimethyl-1,8-digermacyclotetradecane **8** and 1,8-dibromo-1,8-dimethyl-1,8-digermacyclotetradecane **10** is shown in Scheme 2.

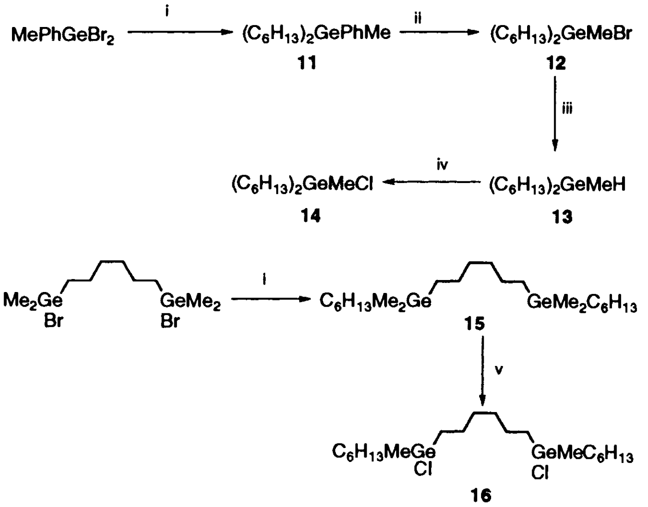
We prepared acyclic organogermanium compounds, chloro(dihexyl)methylgermane **14**, bromo(dihexyl)methylgermane **12** and 1,6-bis[chloro(hexyl)methylgermyl]hexane **16** as acyclic model compounds for anion transport. The strategy employed is given in Scheme 3.

Anion transport capability was examined for most of the organogermanium compounds prepared, which will be described in a later section.

NMR Spectra.—^{1}H and ^{13}C *NMR spectra.* As is the case with organosilicon compounds, protons and carbons bonded or located close to germanium nuclei resonate at a lower frequency, which is very useful for the identification of the structure. The data are consistent with the previously published results for related compounds.[1]



Scheme 2 Synthetic route to 1,8-dihalo-1,8-dimethyl-1,8-digermacyclotetradecanes **8**, **10**. *Reagents and conditions:* i, $SnCl_4$ $MeNO_2$, reflux, 5 h; ii, LAH–Et_2O, reflux, 3 h; iii, Br_2–$CHCl_3$, room temp., 3 h.



Scheme 3 Synthetic route to methyl(dihexyl)halogermanes **12**, **14** and bis[chloro(hexyl)methylgermyl]hexane **16**. *Reagents and conditions:* i, $C_6H_{13}MgBr$–Et_2O, reflux, 3 h; ii, Br_2–EtBr; iii, LAH–Et_2O, reflux, 3 h; iv, CCl_4, reflux, 5 h; v, $SnCl_4$–$MeNO_2$, reflux, 5 h.

The ^{13}C chemical shift data of **4–10** are summarized in Table 1. ^{13}C chemical shifts of reference compounds **14** and **16** together with their precursors are given in the Experimental section.

^{73}Ge *NMR spectra*. The measurement of ^{73}Ge (a quadrupolar nucleus; quadrupolar moment $q = -0.2$) NMR spectra is generally difficult because of excessive line broadening unless the germanium atom is symmetrically substituted. This broadening occurs through the interaction of the electric field gradient at the nucleus with the quadrupolar moment of germanium. Thus, in the absence of chemical exchange processes, the extent of line broadening may be related to the local symmetry at the germanium centre.

Of the halo- and phenyl-substituted germanes, only highly symmetrical tetrahalogermanes and tetraarylgermanes[6] exhibited narrow ^{73}Ge signals. Since ^{73}Ge chemical shifts can be a very good indicator of hypervalency,[7] we attempted to determine ^{73}Ge chemical shifts of **4–6**, **8–10** with the aid of a high-frequency instrument which is expected to have a much better sensitivity than the instruments used in previous studies (*e.g.*, JEOL FX-90Q with low-frequency insert[8]). Unfortunately, compounds unsymmetrically substituted with halogen(s) on germanium failed to show any signal as was previously noted.

The newly obtained data for **4** and **9** are included in Table 1 for reference. The values for **4** (δ -9; the half-width $\nu_{1/2}$ = 470 Hz) in contrast to the values for 1,1-diphenylgermacyclohexane (δ -33; $\nu_{1/2}$ = 370 Hz)[9] is in line with the corresponding pair, **7** (δ +5; $\nu_{1/2}$ = 35 Hz)[1] and 1,1-dimethylgermacyclohexane (δ -13.7; $\nu_{1/2}$ = 22 Hz).[8]

The shifts for **4** and **7** reflect the C–Ge–C angles which are close to tetrahedral [GeMe4 (δ 0)]. The line-widths of **4** and **7** are also very informative. It was established that the line-width is a good indication of relaxation times for alkylgermanes, and that the correlation times (hence the relaxation times) are related to molecular radius.[10] The relaxation times of **4** and **7** are expected to be much shorter (hence the line-widths are much larger) than those of corresponding germacyclohexane derivatives unless the extent of asymmetry of the electric field gradient around germanium is essentially identical for germamacrocycles and germacyclohexanes. Thus, the observed line-widths of **4** and **7** are a very good indication of higher symmetry around germanium of **4** and **7**.

Anion Migration Experiments.—To estimate the anion transport capability of organogermanium compounds, the so-called U-tube test[11] (Fig. 1) was attempted. Thus, in the bottom part of the U-tube,* was placed a methylene chloride solution of 1,8-digermacyclotetradecanes (0.05 mol dm^{-3}; 0.7 cm^3 = 3.5 mmol) and in the right arm of U-tube, aqueous tetrabutylammonium chloride or bromide (1.5 mol dm^3; 0.2 cm^3 = 0.3 mmol) was added. In the left arm of the U-tube was placed pure H_2O. A small magnetic bar was placed in the bottom of each arm and the mixture was stirred. 0.25 mm^3 portions of H_2O were taken from the left arm by means of a syringe at intervals and the number of anions transported was determined by means of ion chromatography. The analysis was attempted for 40 h. By this time, the presence of halogens from the decomposed germanium compounds began to obscure the anion transport analysis. A blank test was also performed where no germamacrocycle was dissolved in the organic layer. No anion was detected in the water in the left arm.

We previously found out that **7** did not exhibit any anion transport capability. We expected that **4** might transfer anions since it is generally accepted that an aryl substituent increases the Lewis acidity of a group 14 element.[12] To our disappointment, however, **4** failed to transport any halide which indicates that enhanced acidity is required for anion transport.

Compounds **5** and **6**, which certainly possess enhanced Lewis acidity associated with germanium, slowly decomposed under the experimental conditions of the U-tube test. Thus, it is impossible to estimate the anion migrating capability of these compounds though we believe that the Lewis acidity would be larger than that of **4** or **7**.

We expected to be able to estimate the anion transport capability of compounds **8** and **10** since these must be less susceptible to hydrolysis and yet have enhanced Lewis acidity as compared with **4** and **7**. Indeed, **8** effectively transferred chloride, the amount of which increased linearly with time and after 40 h about 18%† chloride had been transferred (Fig. 2). The rate of transport of bromide anion by **8** was slower, and 5% had been transported after 40 h under similar conditions (Fig. 3).

A similar result was observed when a mixture of tetramethylammonium chloride (1.5 mol dm^{-3}) and bromide (1.5 mol dm^{-3}) was used. 10.5% chloride was transferred after 40 h while the amount of bromide transported was about 4% (Fig. 4).

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* The original U-tube was modified to H-tube so that a small magnetic bar could be used to affect the mixing.

† Since the transport is an equilibrium process, the anion concentration of the aqueous layer of the right- and left-arms will eventually be equal. The percentage transport is referred to this equilibrium state (100%). Hence, 18% transport corresponds to migration of 9% anion initially taken.

Table 1 ^{73}Ge^a and ^{13}C^b NMR chemical shifts of 1,8-digermacyclotetradecanes and related compounds

	Ge	Cα	Cβ	Cγ	Me	Phenyl
4 (Ph, Ph)	−9	11.0	21.9	29.9	—	139.0 (*i*), 134.2 (*o*), 128.0 (*p*), 128.5 (*m*)
5 (Cl, Cl)		22.0	25.4	29.3	—	—
6 (Br, Br)		22.7	27.2	28.9	—	—
7 (Me, Me)^c	5.0	13.9	22.5	30.2	−3.9	—
8 (Me, Cl)		18.9	21.8	29.4	2.1	
9 (Me, H)	−43.8	13.2	24.9	31.4	−5.1	—
		11.7	23.3	30.0	−6.7	
10 (Me, Br)		19.2	21.9	29.6	2.6	—
		19.3	22.2	29.3	2.6	

^{a} In ppm relative to external GeMe$_4$ (δ 0). ^{b} In ppm relative to internal SiMe$_4$ (δ 0). ^{c} Data taken from ref. 1.

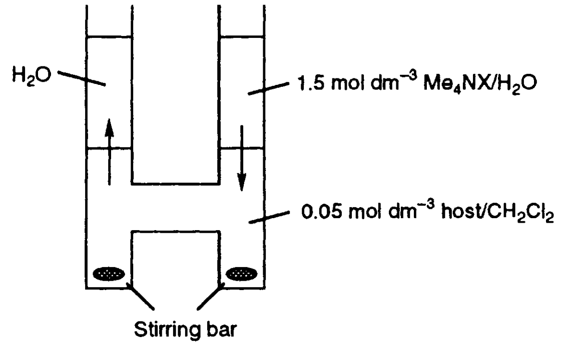

Fig. 1 H-Tube for transport test, host = 1,8-digermacyclotetradecane, X = Cl or Br

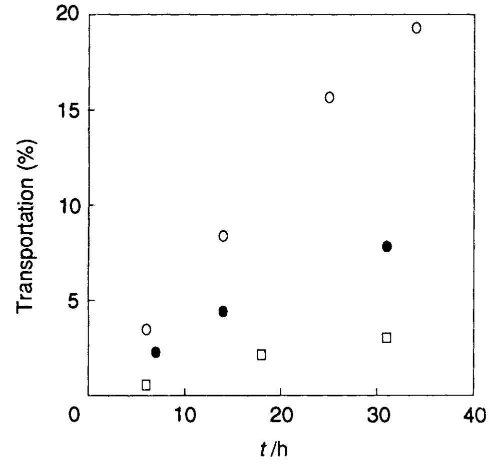

Fig. 2 Time dependence of Me$_4$NCl transport: ○, **8**; ●, **14**; □, **16**

These values can be compared with a similar U-tube test[13] for a crown ether derivative as the carrier of sodium and potassium cations which typically gives some 10% transport of potassium ion after 40 days.

The selectivity, *i.e.*, the transport ratio (Cl$^-$: Br$^-$), achieved by **8**, was 3.3 : 1 in a separate experiment while it was 2.7 : 1 when a mixture of the two anions was used. In the case of the crown ether mentioned above, the transport ratio (K$^+$: Na$^+$) was as high as 71 : 1. In this case the high selectivity was achieved at the expense of the speed of transport. Taking all things into consideration, it can be concluded that germamacrocycle **8** is an efficient and selective carrier of chloride though there is room for improvement in the selectivity.

The behaviour of **10** was a little difficult to examine since slow hydrolysis occurred concomitantly during the transfer experiment which obscured the result for bromide transfer. As far as the chloride transfer is concerned, the effectiveness was of the same order as that of **8**.

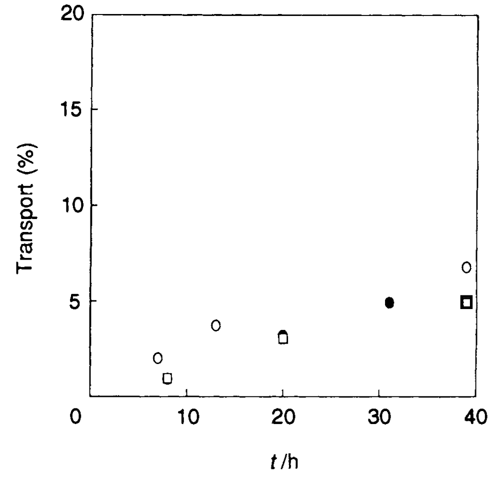

Fig. 3 Time dependence of Me$_4$NBr transport: ○, **8**; ●, **14**; □, **16**

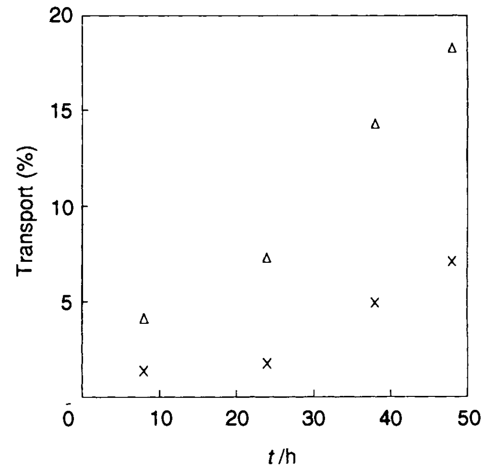

Fig. 4 Time dependence of transport by **8** (competitive Me$_4$NCl/Me$_4$NBr): △, Cl$^-$; ×, Br$^-$

Mechanism of Transport.—In view of the size of the cavity of 1,8-digermacyclotetradecanes, transport necessarily involves some kind of complexation between the host germacycles and a halide. Two questions arise before the detailed mechanism of the transport can be discussed. One is whether the ring structure is a necessary condition of transport, and the other is whether the presence of two or more germanium moieties is a necessary condition.

To clarify these points, we prepared two model compounds, dihexyl(methyl)chlorogermane **14** and 1,6-bis[methyl(hexyl)-chlorogermyl]hexane **16**. Compound **14** is a very poor carrier, and only 3.2% chloride was transported after 40 h, while **16** is more effective, transporting 8.5%, about half the value for **8**, of chloride after 40 h. This observation indicates that the presence of two germanium nuclei and the ring structure both play an important role in the anion transport. As for the transport of bromide, both **14** and **16** transport the anion as much as **8** does which indicates that these structural features also determine the selectivity.

Conclusions

We conclude that **8** can selectively transfer Cl^- from a mixture of Cl^- and Br^-. This is the first example of selective anion transfer capability shown by an organogermanium compound. Attempts to improve the selectivity and to isolate the complexes between germacycles and halide are being made in our laboratory.

Experimental

^1H, ^{13}C and ^{73}Ge NMR spectra were determined for solutions in $CDCl_3$ or C_6D_6 [*ca.* 1% v/v for ^1H, ^{13}C and 1 : 4 (solvent) v/v for ^{73}Ge] on a JEOL α-500 spectrometer operating at 500.00, 125.65 and 17.30 MHz, respectively, at 30 °C. For ^1H and ^{13}C measurements, 5 mm tubes were used while for ^{73}Ge measurements, 10 mm tubes were employed. Typical measurement conditions were as follows: (^1H) pulse width, 5.65 μs (45°); spectral width, 4500 Hz; number of scans, 8; pulse delay, 2.72 s; data points, 32 768: (^{13}C) pulse width, 4.70 μs (45°); spectral width, 19 000 Hz; number of scans, 100; pulse delay, 1.48 s; data points, 32 768: (^{73}Ge) pulse width, 40 μs (90°); spectral width, 7000–25 000 Hz; number of scans, 10 000; pulse delay, 0.04 s; data points, 2048.

Ion chromatography. Ion chromatography was carried out with a Waters system at 35 °C (510 HLPC pump and 430 conductivity detector). The column used was a Waters IC-PAK A with borate buffer as the eluent.

Synthesis of 1,1,8,8-*Tetrahalo*-1,8-*digermacyclotetradecanes*.—A solution of bromodiphenylgermane (20 g, 8.7 mmol) and hexa-1,5-diene (3.5 g, 4.3 mmol) in hexane (100 cm^3) was refluxed for 5 h. The solvent was removed and the excess bromodiphenylgermane was removed *in vacuo* to afford crude 1,6-bis(bromodiphenylgermyl)hexane **1** (16 g, 71%); δ_H(500 MHz, $CDCl_3$) 1.23–1.96 (12 H, m, CH_2) and 7.34–7.75 (20 H, m, Ph); δ_C(125.65 MHz, $CDCl_3$) 19.3 (t, CH_2), 24.2 (t, CH_2), 31.7 (t, CH_2), 128.5 (d, *m*-C), 128.8 (d, *p*-C), 133.6 (d, *o*-C) and 135.8 (s, *ipso*-C).

To a solution of lithium aluminium hydride (LAH) (0.5 g, 13 mmol) in dry diethyl ether (30 cm^3), a solution of crude **1** (10.0 g, 14 mmol) in diethyl ether (30 cm^3) was added dropwise, and the mixture was refluxed for 3 h. On removal of the solvent white crystals of 1,6-bis(diphenylgermyl)hexane **2** (5.8 g, 75%), m.p. 74–75 °C, were obtained (Found: C, 66.80; H, 6.54. Calc. for $C_{30}H_{34}Ge_2$: C, 66.67; H, 6.35%); δ_H(500 MHz, $CDCl_3$) 1.24–1.64 (12 H, m, CH_2), 5.0 (2 H, s, GeH) and 7.20–7.62 (20 H, m, Ph); δ_C(125.65 MHz, $CDCl_3$) 13.4 (t, CH_2), 25.7 (t, CH_2), 32.3 (t, CH_2), 128.2 (d, *m*-C), 128.8 (d, *p*-C), 134.7 (d, *o*-C) and 137.0 (s, *ipso*-C).

The tetraphenyl compound **2** (10 g, 18.6 mmol) was dissolved in CCl_4 and refluxed for 3 h. On removal of the solvent, 1,6-bis(chlorodiphenylgermyl)hexane **3** (11.3 g, 100%), m.p. 90–91 °C, was obtained quantitatively as a white solid. (Found C, 59.28; H, 5.45. Calc. for $C_{30}H_{32}Cl_2Ge_2$: C, 59.20; H, 5.30%); δ_H(500 MHz, $CDCl_3$) 1.26–1.64 (12 H, m, CH_2) and 7.36–7.60 (20 H, m, Ph); δ_C(125.65 MHz, $CDCl_3$) 18.8 (t, CH_2), 23.8 (t, CH_2), 31.8 (t, CH_2), 128.6 (d, *m*-C), 130.2 (d, *p*-C), 133.5 (d, *o*-C) and 136.1 (s, *ipso*-C).

1,1,8,8-*Tetraphenyl*-1,8-*digermacyclotetradecane* **4**. The dichloride **3** (2.0 g, 3.2 mmol) was dissolved in THF (10 cm^3), to which fine chips of lithium (0.46 g, 100 mmol) were added. An exothermic reaction took place. When the generation of heat ceased, the mixture was refluxed for 30 m and then further stirred for 12 h to complete the formation of the bis-lithio derivative of **3**. The volume of the solution of germyllithium compound was made up to 160 cm^3.

1,6-Dibromohexane (1.0 g, 4.0 mmol) was dissolved in THF (160 cm^3) and ice-cooled, and a THF solution of germyllithium was added dropwise over 2 h. The mixture was further stirred for 36 h at room temp. About one third of the solvent was removed under reduced pressure, and the residue was hydrolysed by means of hydrochloric acid (2 mol dm^{-3}, 100 cm^3). Diethyl ether (200 cm^3) was added, the mixture was washed with water and the organic layer was separated and dried over $MgSO_4$. After removal of the solvent *in vacuo*, the residue was chromatographed on a silica gel column with hexane as the eluent. The material obtained was further chromatographed (reversed phase) with acetonitrile as the eluent, and the main fraction was recrystallized from toluene to afford colourless prisms of **4** (0.16 g, 8%), m.p. 171–172 °C. (Found: C, 69.41; H, 7.02. Calc. for $C_{36}H_{44}Ge_2$: C, 69.53; H, 7.13%); δ_H(500 MHz, $CDCl_3$) 1.18–1.26 (24 H, m, CH_2) and 7.22–7.50 (20 H, m, Ph).

1,1,8,8-*Tetrachloro*-1,8-*digermacyclotetradecane* **5**. The tetraphenyl compound **4** (0.1 g, 0.16 mmol) was dissolved in benzene (10 cm^3) and a catalytic amount of $AlCl_3$ was added.[14] Hydrogen chloride was introduced into the solution for 5 h. The inorganic precipitate was filtered off, and the solvent was removed *in vacuo* to afford tetrachloride **5** (0.042 g, 57%), m.p. 162–165 °C (Found: C,32.54; H, 5.29. Calc. for $C_{12}H_{24}Cl_4Ge_2$: C, 31.66; H, 5.31%)*; δ_H(500 MHz, $CDCl_3$) 1.20–1.83 (24 H, m, CH_2).

1,1,8,8-*Tetrabromo*-1,8-*digermacyclotetradecane* **6**. The tetraphenyl compound **4** (0.10 g, 0.16 mmol) was dissolved in 1,2-dibromomethane (10 cm^3), and a solution of bromine (0.16 g, 1.0 mmol) in 1,2-dibromoethane (10 cm^3) was added dropwise.[15] Refluxing at 80 °C was continued for 5 h. The solvent and excess bromine were removed *in vacuo* to afford the tetrabromo compound (0.066 g, 65%), m.p. 205–206 °C as colourless prisms. (Found: C, 22.68; H, 3.64. Calc. for $C_{12}H_{24}Br_4Ge_2$: C, 22.77; H, 3.64%); δ_H(500 MHz, $CDCl_3$) 1.22–1.92 (24 H, m, CH_2).

Synthesis of 1,8-*Dihalo*-1,8-*dimethyl*-1,1,8,8-*digermacyclotetradecanes*.—The synthesis of 1,1,8,8-tetramethyl-1,8-digermacyclotetradecane **7** has been reported.[1]

1,8-*Dichloro*-1,8-*dimethyl*-1,8-*digermacyclotetradecane* **8**. A mixture of **7** (0.5 g, 1.3 mmol) and anhydrous $SnCl_4$ (1.0 g, 3.8 mmol) in nitromethane (32 cm^3) was heated to reflux for 5 h.[16] The solvent and Sn compounds (mostly $MeSnCl_3$) were distilled *in vacuo* from the cooled reaction mixture and the residue was dried at 0.1 mmHg at room temp. to afford white crystals of **8** (0.48 g, 87%), m.p. 134–135 °C (Found: C, 40.86; H, 7.18. Calc. for $C_{14}H_{30}Cl_2Ge_2$: C, 40.57; H, 7.30%); δ_H(500 MHz, $CDCl_3$) 0.66 (6 H, s, Me), 1.09–1.16 (4 H, m, CH_2), 1.24–1.30 (4 H, m, CH_2) and 1.40–1.53 (16 H, m, CH_2).

1,8-*Dimethyl*-1,8-*digermacyclotetradecane* **9**. A mixture of **8** (200 mg, 0.48 mmol) and LAH (20 mg, 0.53 mmol) in diethyl ether (20 cm^3) was heated to reflux for 3 h. The mixture was cooled and water was slowly added to decompose excess LAH. The organic layer was separated, washed with water, dried and evaporated. The residue solidified upon standing, and was

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* Attempts were made to purify the sample by various means without further success. It seems that a small amount of starting material remained which was impossible to remove.

recrystallized to give colourless prisms of dimethyl compound **9**. (1.5 g, 81%), m.p. 45–46 °C (Found: C, 48.55; H, 9.13. Calc. for $C_{14}H_{32}Ge_2$: C, 48.26; H, 9.33%); δ_H(500 MHz, $CDCl_3$) 0.16 (6 H, s, Me), 0.72–0.88 (8 H, m), 1.28–1.46 (16 H, m, CH_2) and 3.78 (2 H, m, GeH).

1,8-*Dibromo*-1,8-*dimethyl*-1,8-*digermacyclotetradecane* **10**. Complex **4** (100 mg, 0.29 mmol) was dissolved in hexane (20 cm^3), Br_2 (120 mg, 0.75 mmol) in hexane (20 cm^3) was added dropwise with ice-cooling, and the mixture was stirred for 2 h. The usual work-up afforded the title compound, which was recrystallized from $CHCl_3$ to afford colourless needles of **10** (120 mg, 82%), m.p. 127 °C (Found: C, 33.19; H, 4.74. Calc. for $C_{14}H_{32}Br_2Ge_2$: C, 33.41; H, 6.01%); δ_H(500 MHz, $CDCl_3$) 0.78 (6 H, s, Me), 1.16–1.25 (4 H, m, CH_2), 1.29–1.38 (4 H, m, CH_2), 1.40–1.55 (16 H, m, CH_2).

Synthesis of Dihexylgermanes.*—To a Grignard reagent prepared from hexyl bromide (25 g, 151 mmol) in dry diethyl ether (100 cm^3) and Mg turnings (3.7 g, 152 mmol) was added dibromo(methyl)phenylgermane (23 g, 71 mmol) in diethyl ether (100 cm^3) with stirring. Refluxing was continued for 3 h and the mixture was decomposed with aq. HCl (3 mol dm^{-3}). The organic layer was separated, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was distilled *in vacuo* to give dihexyl(methyl)phenylgermane **11** (17.5 g, 68%), b.p. 142–143 °C/2 mmHg; δ_H(500 MHz, $CDCl_3$) 0.33 (3 H, s, Me), 0.86 (6 H, t, Me), 0.94–0.97 (4 H, m, CH_2), 1.24–1.40 (16 H, m, CH_2) and 7.22–7.44 (5 H, m, Ph); δ_C(125.65 MHz, $CDCl_3$) −5.9 (q, Me), 14.1 (q, Me), 14.6 (t, CH_2), 22.6 (t, CH_2), 25.0 (t, CH_2), 31.5 (t, CH_2), 33.1 (t, CH_2), 127.8 (d, *m*-C), 128.1 (d, *p*-C), 133.5 (d, *o*-C) and 141.4 (s, *ipso*-C).

To **11** (17 g, 52 mmol) in ethyl bromide (100 cm^3) was added Br_2 (2.8 cm^3, 54 mmol) in ethyl bromide (30 cm^3). Refluxing was continued for 30 min with stirring, after which the excess bromine, the solvent and bromobenzene formed were distilled off under reduced pressure. The residue was distilled *in vacuo* to afford bromo(dihexyl)methylgermane **12** (15 g, 85%), b.p. 104 °C/4 mmHg; δ_H(500 MHz, $CDCl_3$) 0.63 (3 H, s, Me), 0.89 (6 H, t, Me), 1.11–1.20 (4 H, m, CH_2), 1.21–1.40 (12 H, m, CH_2) and 0.42–1.55 (4 H, m, CH_2); δ_C(125.65 MHz, $CDCl_3$) 2.1 (q, Me), 14.1 (q, Me), 20.9 (t, CH_2), 22.5 (t, CH_2), 24.4 (t, CH_2), 31.4 (t, CH_2) and 32.2 (t, CH_2).

To an ethereal solution of LAH (0.5 g, 13 mmol) in diethyl ether (50 cm^3) was added **12** (7 g, 21 mmol) in diethyl ether (50 cm^3) dropwise. The mixture was refluxed for 3 h and slowly hydrolysed with H_2O, and allowed to stand until the salt formed precipitated and the ethereal layer became clear. The ethereal layer was dried with $MgSO_4$, and the salts were filtered off. The ether was removed under reduced pressure and the residue was distilled *in vacuo* to afford dihexyl(methyl)germane **13** (4.5 g, 84%), b.p. 84 °C/4 mmHg; ν_{max}/cm^{-1} 2000 (GeH); δ_H(500 MHz, C_6D_6) 0.26 (3 H, s, Me), 0.75–1.58 (26 H, m, CH_2 and Me) and 4.07 (1 H, br s, GeH); δ_C(125.65 MHz, C_6D_6) −6.8 (q, Me), 13.8 (q, Me), 14.3 (t, CH_2), 23.0 (t, CH_2), 26.5 (t, CH_2), 31.9 (t, CH_2) and 33.1 (t, CH_2).

The hydride **13** (2.5 g, 9.7 mmol) was dissolved in CCl_4 (50 cm^3) and a catalytic amount of $PdCl_2$ was added. The mixture was refluxed for 3 h. The solvent was removed and the residue was distilled *in vacuo* to afford chloro(dihexyl)methylgermane **14** (2.3 g, 81%), b.p. 99 °C/3 mmHg; δ_H(500 MHz, $CDCl_3$) 0.75 (3 H, s, Me), 0.86 (6 H, t, Me), 1.19–1.38 (16 H, m, CH_2) and 1.46–1.54 (4 H, m, CH_2); δ_C(125.65 MHz, $CDCl_3$) 1.5 (q, Me), 14.1 (q, Me), 20.5 (t, CH_2), 22.5 (t, CH_2), 23.9 (t, CH_2), 31.4 (t, CH_2) and 32.3 (t, CH_2).

Synthesis of 1,6-*Bis*(*hexylgermyl*)*hexanes*.—To an ethereal solution (10 cm^3) of 1,6-bis[bromo(dimethyl)germyl]hexane (3.0 g, 6.7 mmol)[1] was added the Grignard reagent prepared from hexyl bromide (3.0 g, 18 mmol) and magnesium turnings (0.5 g, 20 mmol) in diethyl ether (30 cm^3). The mixture was refluxed for 3 h, decomposed with HCl (2 mol dm^{-3}) and washed with diethyl ether. The ethereal layer was dried with $MgSO_4$, the solvent was removed under reduced pressure and the residue was distilled *in vacuo* (Kugelrohr) to afford 1,6-bis[dimethyl(hexyl)germyl]hexane **15** (2.6 g, 83%), b.p. 170–180 °C/0.5 mmHg; δ_H(500 MHz, $CDCl_3$) 0.08 (12 H, s, Me), 0.66–0.70 (8 H, m, CH_2), 0.88 (6 H, t, Me) and 1.15–1.55 (24 H, m, CH_2); δ_C(125.65 MHz, $CDCl_3$) −4.1 (q, Me), 14.2 (q, Me), 15.6 (t, CH_2), 15.6 (t, CH_2), 22.7 (t, CH_2), 25.1 (t, CH_2), 25.1 (t, CH_2), 31.6 (t, CH_2), 33.1 (t, CH_2) and 33.1 (t, CH_2).

A solution of **15** (1.3 g, 2.8 mmol) and $SnCl_4$ (1.5 g, 5.8 mmol) in nitromethane (20 cm^3) was refluxed for 5 h. The solvent and volatile fraction was removed under reduced pressure and the residue was distilled *in vacuo* (Kugelrohr) to afford 1,6-bis[chloro(methyl)hexylgermyl]hexane **16** (1.1 g, 79%), b.p. 220–230 °C/0.5 mmHg; δ_H(500 MHz, $CDCl_3$) 0.62 (6 H, s, Me), 0.88 (6 H, t, Me), 1.08–1.23 (8 H, m, CH_2), 1.23–1.38 (16 H, m, CH_2) and 1.43–1.55 (8 H, m, CH_2); δ_C(125.65 MHz, $CDCl_3$) 1.5 (q, Me), 14.1 (q, Me), 20.4 (t, CH_2), 20.5 (t, CH_2), 22.5 (t, CH_2), 23.9 (t, CH_2), 24.0 (t, CH_2), 31.4 (t, CH_2), 32.2 (t, CH_2) and 32.3 (t, CH_2).

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