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# Synthesis of polymetallacycloalkanes

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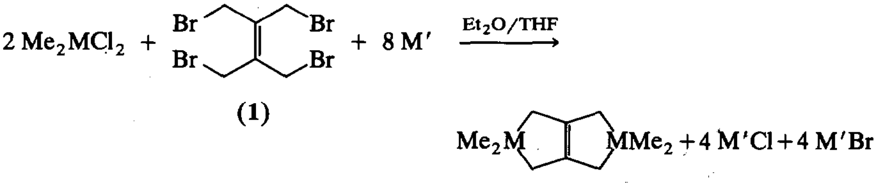
## Abstract

In the reduction of a mixture of an organosilicon or organogermanium dihalide and 1,4-dibromo-2,3-bis(bromomethyl)-2-butene with an alkali metal forming hexahydrodimetallapentalenes, best yields were obtained by using lithium in ether/tetrahydrofuran. This reaction, when extended to 1,2-dichloro-disilanes and -digermanes gave the corresponding tetrametallaoctahydronaphthalenes. When activated zinc was used instead of alkali metal in these reactions, bis(methylene)metallacycloalkanes were formed; their reactions with germanium diiodide gave bicyclic compounds with two or three metal atoms per molecule. A stepwise reaction gave chains of organogermanium bicyclic compounds of controlled length.

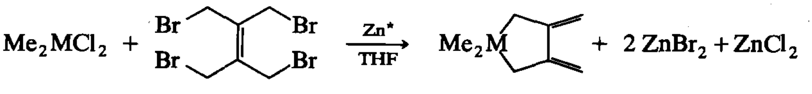
## Introduction

We observed recently [1] that the reduction of a mixture of tetrabromide **1** and dimethyldichlorosilane or dimethyldichlorogermane leads to the formation of hexahydrodimetallapentalenes [2] (eq. 1) or bis(methylene)metallacyclopentanes (eq. 2)



(1)

(M = Si (**2a**), Ge (**2b**);
M' = Li, Na, or K)



(2)

(M = Si (**3a**), Ge (**3b**))

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depending on the nature of the reducing metal. These reactions were used to synthesize new organosilicon and organogermanium cyclic compounds containing two, three or four metal atoms per molecule.

## Results and discussion

The reduction of a mixture of dimethyldichloro-silane or -germane and tetrabromide **1** with an alkali metal (eq. 1) was found to depend on several factors, especially the nature of the solvent and of the alkali metal. With dimethyldichlorosilane and using finely-cut lithium, the reaction was very slow in diethyl ether; after 3 h stirring, only a small amount of lithium halide was formed and most of the lithium remained unchanged. When a mixture of ether/tetrahydrofuran was used, the speed of the reaction increased with the percentage of THF in the mixture. In pure THF, the reaction was fast and exothermic, and lithium was rapidly consumed. However, the yield of the organosilicon bicyclic compound did not increase with the proportion of THF, but passed through a sharp maximum at about 20% THF (Fig. 1).

With sodium, the reaction was also very slow in diethyl ether and the yield was small. By increasing the percentage of THF in the solvent mixture, the yield increased steadily to a plateau at about 70% THF (Fig. 1). With potassium and pure THF, the reaction was fast and exothermic but the yield of the bicyclic compound was very small and the formation of polymers predominant.

When dimethyldichlorogermane was used with lithium as reducing metal, the yield of **2b** also depended on the composition of the solvent, but, in this case the maximum was less sharp than for the silicon analogue and the peak was at a higher THF percentage (40%) (Fig. 1). The maximum yield was lower for the germanium compound (26%) than for the silicon analogue (36%). For a given solvent mixture, the yield of **2** was found to depend also on the concentration and molar ratio of the reagents.

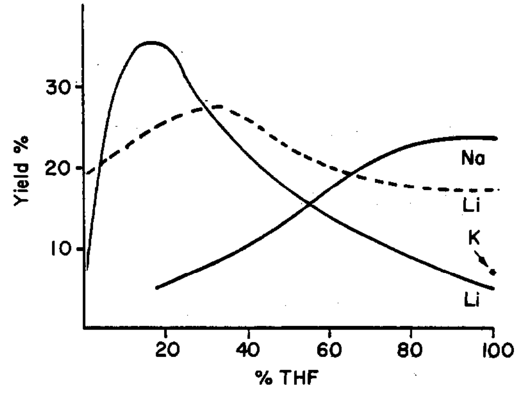
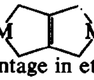
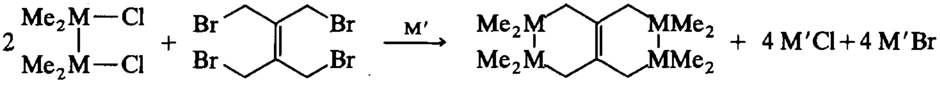


Fig. 1. Yield (%) of $Me_2M$$MMe_2$, for Li, Na, or K (M = Si), and for Li (M = Ge, dotted line), as a function of THF percentage in ether/THF mixture.

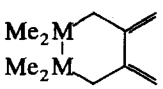
With optimal conditions for cyclization, the new tetrametallaoctahydronaphthalenes **4a,4b** were synthesized (eq. 3).



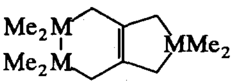
(3)

(M' = Li(Et$_2$O-THF) Na(THF)) (M = Si (**4a**), Ge (**4b**))

These reactions were more complex and several by-products, such as bis(methylene) dimetallacyclohexanes **6a,6b** and trimetallahexahydroindenes **9a,9b** were detected and characterized by comparison with NMR and mass spectra of authentic samples prepared according to eqs. 5 and 9. Bis(methylenes) **6a,6b** were formed in lower yield when lithium was used instead of sodium.

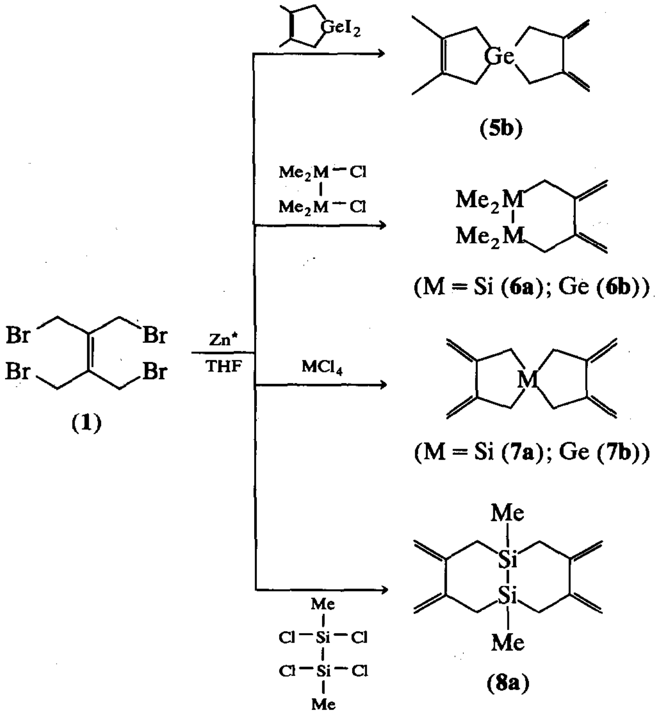


(M = Si (**6a**), Ge (**6b**))



(M = Si (**9a**), Ge (**9b**))

Bis(methylene)metallacycloalkanes were obtained when mixtures of **1** and silicon or germanium polyhalides were reduced with activated zinc in THF solution.



(4)

(**5b**)

(5)

(M = Si (**6a**); Ge (**6b**))

(**1**)

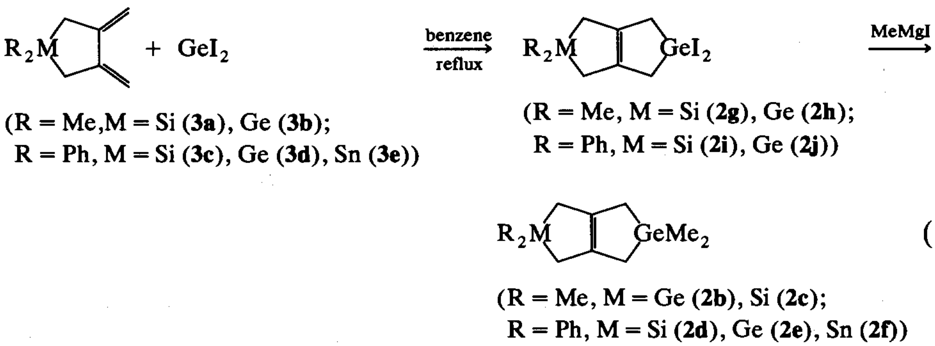
(6)

(M = Si (**7a**); Ge (**7b**))

(7)

(**8a**)

These products are good starting compounds for the synthesis of polycyclic metallacycloalkanes. Bis(methylene)metallacyclopentanes reacted quantitatively with germanium diiodide in boiling benzene (eq. 8).



(R = Me, M = Si (**3a**), Ge (**3b**);
R = Ph, M = Si (**3c**), Ge (**3d**), Sn (**3e**))

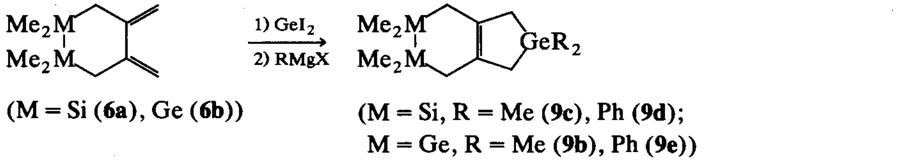
(R = Me, M = Si (**2g**), Ge (**2h**);
R = Ph, M = Si (**2i**), Ge (**2j**))

(8)

(R = Me, M = Ge (**2b**), Si (**2c**);
R = Ph, M = Si (**2d**), Ge (**2e**), Sn (**2f**))

Compound **2b** prepared as above was identical to the product resulting from the reduction of a mixture of dimethyldichlorogermane and tetrabromide **1** with lithium in ether/THF mixture according to the eq. 1. With M = Si or Sn, reaction 8 gave unsymmetrical dimetallahexahydropentalenes.

Similarly, 4,5-bis(methylene)-1,2-dimetallacyclohexanes gave an almost quantitative cycloaddition with germanium diiodide resulting in bicyclic compounds having three metal atoms per molecule (eq. 9).

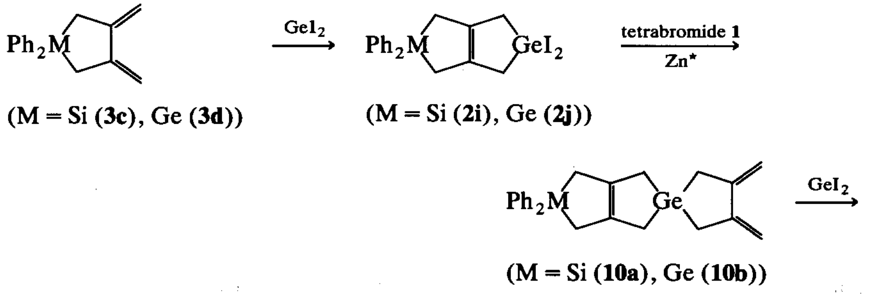


(9)

(M = Si (**6a**), Ge (**6b**))

(M = Si, R = Me (**9c**), Ph (**9d**);
M = Ge, R = Me (**9b**), Ph (**9e**))

The bicyclic organogermanium diiodides **2i,2j** resulting from cycloaddition (eq. 8) reacted further, just like dialkyldichlorogermanes, with tetrabromide **1** in the presence of activated zinc to form new bis(methylene) cycloalkanes **10a,10b** which were stable and could be isolated by liquid chromatography. These conjugated dienes reacted quantitatively with a stoichiometric amount of germanium diiodide to give tetracyclic germanium diiodides **11a,11b** which then reacted with tetrabromide **1** in the presence of activated zinc to give the pentacyclic bis(methylenes) **12a,12b** etc.. Therefore, it is possible to build, step by step, a chain of germanium bicycles of any desired length, isolating compounds in each step (eqs. 10–13).

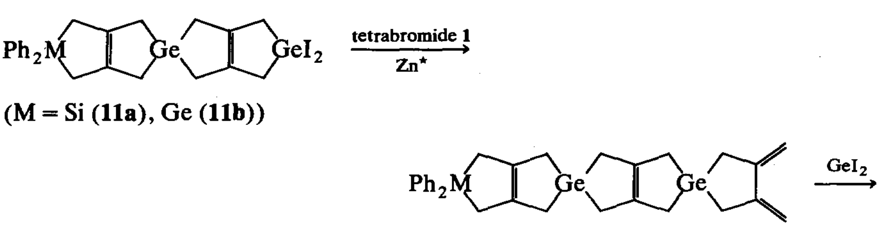


(M = Si (**3c**), Ge (**3d**))

(M = Si (**2i**), Ge (**2j**))

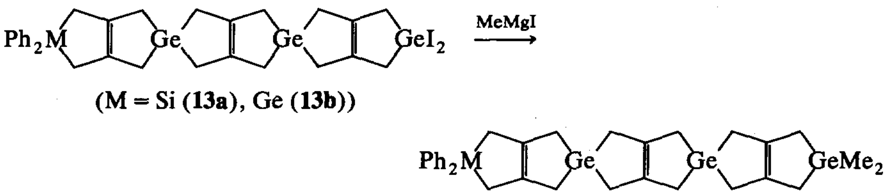
(10)

(M = Si (**10a**), Ge (**10b**))



(M = Si (**11a**), Ge (**11b**))

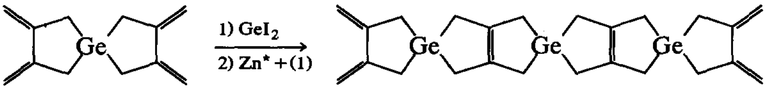
(M = Si (**12a**), Ge (**12b**)) (11)



(M = Si (**13a**), Ge (**13b**))

(M = Si (**14a**), Ge (**14b**)) (12)

Analogous reactions were obtained with tetramethylenes **7**.



(**7b**) (**15**) (13)

## Experimental

*Yield of hexahydrodisilapentalene (2a) as a function of the reducing metal and the solvent used*

*(a) With lithium.* In a series of similar flasks (100 ml) fitted with a reflux condenser and filled with argon was placed a stirring bar and the same amount of finely cut lithium (0.56 g, 0.08 g. atom) and tetrabromide **1** (4.00 g, 10 mmol). To each flask was then added a solution of dimethyldichlorosilane (2.60 g, 20 mmol) in 50 ml diethylether/tetrahydrofuran and the mixtures stirred for 5 h.

The amounts of **2a** in the different flasks, determined by gas chromatography (20% SE30 1/4″ × 5′ column, helium as carrier gas) were the following (% $Et_2O$/THF, rel. area): 100/0, 5; 80/20, 100; 60/40, 60; 40/60, 45; 20/80, 25; 100/0, 18. The maximum yield, obtained with $Et_2O$/THF (80/20 vol.%), was determined by adding 100 ml pentane to this mixture. After filtration through glass wool, the organic solution was washed with water and dried over sodium sulfate. The residue obtained after removal of the solvent was chromatographed on silicagel (230–400 mesh, eluent pentane) giving 0.70 g (3.6 mmol), 36% yield) of pure **2a**. Yields (% THF, yield %); 0, 1.8; 20, 36.0; 40, 21.6; 60, 16.2; 80, 9.0; 100, 6.5.

*(b) With sodium.* In similar experiments using powdered sodium (1.84 g, 0.08 mol) instead of lithium, the yields were (% THF, yield %): 20, 4.8; 50, 17.5; 80, 24; 100, 22.5.

*(c) With potassium.* Only one experiment was carried out using finely-cut potassium (3.12 g, 0.08 mol) in THF. The reaction was fast and potassium

disappeared within 1 h, giving a dark blue mixture. Only a small amount ( ~ 7%) of **2a** was obtained together with a great quantity of polymers.

*Optimization of the synthesis of* ***2a***. The yield of **2a** was also found to depend on the concentration of the reagents and on the molar ratio tetrabromide **1**/$Me_2SiCl_2$. The best yield of **2a** was 44.1%.

### *Yield of hexahydrodigermapentalene* ***2b*** *as a function of the solvent used (lithium as reducing metal)*

In similar experiments but using dimethyldichlorogermane (3.47 g, 20 mmol), tetrabromide **1** (4.00 g, 10 mmol) and lithium (0.56 g, 0.08 g. atom) the following results were obtained as a function of the solvent composition (% $Et_2O$/THF, rel. yields): 100/0, 69; 80/20, 91; 60/40, 100; 40/60, 73; 20/80, 66. Treatment of the mixture containing 40% THF (maximum yield) gave 0.76 g (2.66 mmol, 26.6% yield) of chromatographically pure **2b**. Yields (% THF, yield %); 0, 18.3; 20, 24.2; 40, 26.6; 60, 19.4; 80, 17.5.

### *3,4-Bis(methylene)-1,1-diphenyl-silacyclopentane* (***3c***)

To a stirred suspension of activated zinc powder (10.0 g, 0.15 g. atom) in 10 ml THF was added dropwise a solution of 6.56 g (25.0 mmol) of diphenyldichlorosilane and 10.0 g (25.0 mmol) of tetrabromide **1** in 50 ml THF. After the addition, the mixture was boiled for 3 h. After cooling, pentane (300 ml) was added, the organic solution filtered on Celite, washed ten times with water, dried over sodium sulfate, and the solvent distilled. The residue (8.5 g) was chromatographed on 35 g silica gel (eluent pentane) to give 2.22 g (8.46 mmol) of **3c** as a viscous colourless liquid (33.9%). $n_D^{20} = 1.6039$. IR spectrum $\nu$ ($cm^{-1}$): 3068, 3048 (=$CH_2$); 1626, 1613, 1589 (C=C). $^1H$ NMR spectrum (80 MHz, $CDCl_3$): $\delta$ (ppm): 2.21 (t, 4H, $CH_2Si$); 4.90 (q, 2H, C=$CH_2$); 5.37 (q, 2H, C=$CH_2$); 7.30–7.65 (m, 10H, $C_6H_5$). Anal. Found: C, 82.65; H, 6.90. $C_{18}H_{18}Si$ calc.: C, 82.38; H, 6.91%.

Similar reductions gave the following bis(methylene)metallacycloalkanes:

### *3,4-Bis(methylene)-1,1-diphenyl-1-germacyclopentane* (***3d***)

By adding 24.15 g (62.5 mmol) of diphenylgermanium dibromide and 25.0 g (62.5 mmol) of tetrabromide **1** in 125 ml THF to an excess (25.0 g, 0.38 mol) of activated zinc in 25 ml THF and boiling the mixture for 5 h, 11.46 g of residue was obtained. Purification over 30 g silica gel gave 6.87 g (22.4 mmol) of pure **3d**. Yield 35.6%. $n_D^{20} = 1.6130$. IR spectrum: $\nu$ ($cm^{-1}$): 3068 (=$CH_2$), 1624, 1586 (C=C). $^1H$ NMR spectrum (80 MHz, $CDCl_3$): $\delta$ (ppm): 2.26 (s, 4H, $GeCH_2$); 4.86 (m, 2H, C=$CH_2$); 5.26 (m, 2H, C=$CH_2$); 7.40 (m, 10H, $C_6H_5$). Anal. Found: C, 70.08; H, 5.95. $C_{18}H_{18}Ge$ calc.: C, 70.44; H, 5.91%.

### *3,3-Bis(methylene)-1,1-diphenyl-1-stannacyclopentane* (***3e***)

Reduction of 8.60 g (25 mmol) of diphenyltin dichloride and 14.0 g (35 mmol) of **1** with 15 g of powdered zinc in 70 ml THF gave 0.49 g of pure **3e** (5.5%). IR spectrum (KBr, $C_6H_6$): $\nu$ ($cm^{-1}$): 3065, 3050 (=$CH_2$); 1636, 1616 (C=C). $^1H$ NMR spectrum (80 MHz, $CDCl_3$): $\delta$ (ppm): 2.21 (t, 4H, $CH_2Sn$); 4.79 (q, 2H, C=$CH_2$); 5.07 (q, 2H, C=$CH_2$); 7.32–7.55 (m, 10H, $C_6H_5$).

*Reduction of a mixture of tetramethyl-1,2-dichlorodigermane and tetrabromide 1*

*(a) With sodium.* A mixture of tetrabromide **1** (4.0 g, 10 mmol), finely-cut sodium (1.95 g, 0.085 g. atom) and tetramethyl-1,2-dichlorodigermane (5.52 g, 20 mmol) in 40 ml THF was boiled for 4 h. After centrifugation of the dark-blue mixture and usual treatment of the organic phase a clear yellow thick liquid (2.64 g) containing three principal compounds (GC-MS Hewlett-Packard 5989 A, 150–280°C, 20°C/min, 70 eV, *m/e*, rel. int.) was obtained:

*4,5-Bis(methylene)-1,1,2,2-tetramethyl-1,2-digermacyclohexane* (**6b**): 286, 45, ($M^+$); 271, 63, $(M-CH_3)^+$; 169, 51, $(M-GeMe_3)^+$; 119, 100, $(Me_3Ge)^+$; 104, 14, $(Me_2Ge)^+$; 89, 82, $(MeGe)^+$.

*2,3,4,5,6,7-Hexahydro-2,2,5,5,6,6-hexamethyl-1*H*-2,5,6-trigermaindene* (**9b**): 388, 36, ($M^+$); 373, 12, $(M-CH_3)^+$; 271, 9, $(M-CH_3GeMe_2)^+$; 206, 64, $(Me_4Ge_2)^+$; 167, 12; 119, 100, $(Me_3Ge)^+$; 104, 10, $(Me_2Ge)^+$; 89, 52, $(MeGe)^+$.

*2,2,3,3,6,6,7,7-Octamethyl-2,3,6,7-tetragermadecahydronaphthalene* (**4b**): 492, 10 ($M^+$); 477, 23, $(M-CH_3)^+$; 373, 18, $(M-GeMe_3)^+$: 308, 15; 271, 15, $(Me_6Ge_2)^+$; 221, 14; 167, 15; 119, 100, $(Me_3Ge)^+$; 104, 8, $(Me_2Ge)^+$; 89, 50, $(MeGe)^+$.

*(b) With lithium.* A mixture of tetrabromide **1** (4.0 g, 10 mmol), finely-cut lithium (0.59 g, 0.084 g. atom) and tetramethyl-1,2-dichlorodigermane (5.52 g, 20 mmol) was stirred under argon until the lithium was consumed (3 h). After the usual treatment, a viscous liquid (4.23 g) containing polymers, trigermahexahydroindene (**9b**), tetragermadecahydronaphthalene (**4b**) and only traces of bis(methylene)digermacyclohexane (**6b**) was obtained.

*Reduction of a mixture of tetramethyl-1,2-dichlorodisilane and tetrabromide 1*

*(a) With sodium.* A mixture of tetrabromide **1** (4.0 g, 10 mmol), powdered sodium (1.84 g, 0.082 g. atom) and tetramethyl-1,2-dichlorodisilane (3.74 g, 20 mmol) in 50 ml THF was boiled for 8 h giving a dark-blue mixture. After the usual treatment of the organic phase, the following organosilicon compounds were found (GC-MS) in the viscous liquid residue (3.83 g) (*m/e*, rel. int.):

*4,5-Bis(methylene)-1,1,2,2-tetramethyl-1,2-disilacyclohexane* (**6a**): 196, 51, ($M^+$); 181, 80, $(M-CH_3)^+$; 153, 21 $(M-MeSi)^+$; 122, 30 $(M-Me_3SiH)$; 73, 100 $(Me_3Si)^+$.

*2,3,4,5,6,7-Hexahydro-2,2,5,5,6,6-hexamethyl-1*H*-2,5,6-trisilaindene* (**9a**): 254, 97 ($M^+$): 239, 32 $(M-CH_3)^+$; 195, 17 $(M-Me_2SiH)^+$; 181, 25 $(M-Me_3Si)^+$; 133, 25; 116, 37 $(Me_2Si{-}SiMe_2)^+$; 73, 100 $(Me_3Si)^+$.

*2,2,3,3,6,6,7,7-Octamethyl-2,3,6,7-tetrasiladecahydronaphthalene* (**4a**): 312, 89, ($M^+$); 297, $(M-CH_3)^+$; 239, 16, $(M-SiMe_3)^+$; 223, 6; 179, 24; 116, 22 $(Me_2Si{-}SiMe_2)^+$; 73, 100, $(Me_3Si)^+$.

*(b) With lithium.* The reduction of tetrabromide **1** (11 g, 27.5 mmol) and tetramethyl-1,2-dichlorodisilane (10.39 g, 55 mmol) with lithium (1.53 g, 0.22 g. atom) in 50 ml THF gave a mixture containing polymers, hexahydrotrisilaindene (**9a**) and, tetrasiladecahydronaphthalene (**4a**) as principal products and traces of bis(methylene)disilacyclohexane (**6a**) and hexahydrodisilapentalene (**2a**).

*2,3-Dimethyl-7,8-bis(methylene)-5-germaspirol[4,4]non-2-ene* (**5b**)

A mixture of 10.00 g (30.6 mmol) of germanium diiodide and 3.0 g (36 mmol) of 2,3-dimethyl-1,3-butadiene was stirred with gentle heating for 0.5 h. After cooling, addition of dry pentane (50 ml), filtration, and removal of the solvent, the residue (12.39 g, 98.2%) consisted mainly of pure 3,4-dimethyl-1,1-diiodogermacyclopent-3-

ene. This diiodide (30 mmol) and tetrabromide **1** (12.00 g, 30 mmol) in 50 ml THF was added slowly to a stirred suspension of activated zinc (12.0 g, 0.18 g. atom) and the mixture heated under reflux for 5 h. After the usual treatment, the crude product 2.07 g was purified over 30 g silica gel (eluent pentane) giving 0.70 g of pure **5b**. Yield 9.93%, $n_D^{20} = 1.5497$. $^1$H NMR (80 MHz, $CDCl_3$): $\delta$ (ppm): 5.15 (q, 2H, $C{=}CH_2$); 4.75 (q, 2H, $C{=}CH_2$); 1.94 (tr, 4H, $GeCH_2C{=}$); 1.73 (s, 10H, $GeCH_2CCH_3$). IR spectrum (KBr); $\nu$ (cm$^{-1}$): 3077 ($=CH_2$); 1646, 1624, 1615, 1591 (C=C). Anal. Found: C, 61.03; H, 7.45. $C_{12}H_{18}Ge$ calc.: C, 61.37; H, 7.72%.

*4,5-Bis(methylene)-1,1,2,2-tetramethyl-1,2-disilacyclohexane (6a)*

From 4.69 g (25.0 mmol) of 1,2-dichlorotetramethyldisilane [3], 10.0 g (25.0 mmol) of tetrabromide **1** and 10.0 g of zinc in 60 ml THF were obtained 1.78 g (9.05 mmol) of pure **5a**. Yield 36.2%, b.p. 91–92°C/25 mmHg; $n_D^{20} = 1.5010$. IR spectrum: $\nu$(C=C) at 1633, 1615 and 1591 cm$^{-1}$. $^1$H NMR spectrum (80 MHz, $CDCl_3$): $\delta$ (ppm): 0.09 (s, 12H, $CH_3$); 1.74 (d, 4H, $CH_2Si$); 4.55 and 4.85 (m, 4H, $C{=}CH_2$). Anal. Found: C, 61.05; H, 10.02. $C_{10}H_{20}Si_2$ calc.: C, 61.14; H, 10.26%.

*4,5-Bis(methylene)-1,1,2,2-tetramethyl-1,2-digermacyclohexane (6b)*

From 3.33 g (12.06 mmol) of 1,2-dichlorotetramethyldigermane [4], 4.82 g (12.06 mmol) of tetrabromide **1** and 10.0 g of powdered zinc in 35 ml THF were obtained 1.68 g (5.89 mmol) of pure **6b**. Yield 48.8%, $n_D^{20} = 1.5367$; b.p. 67°C/ 1 mmHg. IR spectrum: $\nu$(C=C) at 1635, 1609, 1589 cm$^{-1}$. $^1$H NMR spectrum (80 MHz, $CDCl_3$): $\delta$ (ppm): 0.29 (s, 12H, $CH_3$); 1.93 (d, 4H, $CH_2Ge$, $J = 1.1$ Hz); 4.59 and 4.81 (m, 4H, $C{=}CH_2$). Mass spectrum (70 eV, $m/e$, rel int.): 286, 49, $(M^+)$; 271, 59, $(M - CH_3)^+$; 169, 47, $(M - GeMe_3)^+$; 119, 96, $(Me_3Ge)^+$; 104, 20, $(Me_2Ge)^+$; 89, 100, $(MeGe)^+$.

*2,3,7,8-Tetrakis(methylene)-5-silaspiro[4.4]nonane (7a)*

Reduction of 2.12 g (12.5 mmol) of silicon tetrachloride and 10.0 g (25 mmol) of **1** in 50 ml THF gave 0.11 g (4.6 %) of pure **7a**. IR spectrum (KBr): $\nu$ (cm$^{-1}$): 3078 ($=CH_2$); 1627, 1613, 1597 (C=C). $^1$H NMR spectrum (80 MHz, $CDCl_3$): $\delta$ (ppm): 1.8 (t, 8H, $CH_2Si$); 4.78 (q, 4H, $C{=}CH_2$); 5.25 (q, 4H, $C{=}CH_2$).

*2,3,7,8-Tetrakis(methylene)-5-germaspiro[4.4]nonane (7b)*

Similar reduction of 2.71 g (12.6 mmol) of germanium tetrachloride and 12.0 g (30 mmol) of **1** with 13 g of zinc in 70 ml THF gave, after the usual work-up, 0.68 g of pure **7b** (23.2%); $n_D^{20} = 1.5695$; b.p. 112°C/11 mmHg. IR spectrum (KBr): $\nu$ (cm$^{-1}$): 3078 ($=CH_2$); 1624, 1614, 1592 (C=C). $^1$H NMR spectrum (80 MHz, $CDCl_3$): $\delta$ (ppm): 1.98 (t, 8H, $CH_2Ge$); 4.78 (q, 4H, $C{=}CH_2$); 5.18 (q, 4H, $C{=}CH_2$). Anal. Found: C, 62.28; H, 7.05. $C_{12}H_{16}Ge$ calc.: C, 61.90; H, 6.93%.

*Decahydro-2,5,6,7-tetrakis(methylene)-4a,8a-dimethyl-4a,8a-disilanaphthalene (8a)*

Reduction of a mixture of 2.85 g (12.5 mmol) of 1,2-dimethyl-1,1,2,2-tetrachlorodisilane [5] and 10.0 g (25.0 mmol) of **1** with 12 g of activated zinc in 50 ml THF gave 0.25 g of pure **8a** (8.2%) as a mixture of isomers (*cis/trans* = 3), $n_D^{20} = 1.5489$. IR spectrum (KBr): $\nu$ (cm$^{-1}$): 3078 ($=CH_2$); 1625, 1613, 1591 (C=C). $^1$H NMR spectrum (80 MHz, $CDCl_3$): $\delta$ (ppm): *cis*-isomer: 0.20 (s, 6H, $CH_3$); 1.75 (m, 8H, CH$_2$Si); 4.76 (m, 4H, C=CH$_2$); *trans*-isomer: 0.16 (s, 6H, CH$_3$); 1.84 (m, 8H, CH$_2$Si); 4.62 (m, 4H, C=CH$_2$); 4.82 (m, 4H, C=CH$_2$).

### *2,3,4,5,6,7-Hexahydro-2,2,5,5,6,6-hexamethyl-1*H*-2,5,6-trigermaindene* (**9b**)

A mixture of 2.24 g (7.85 mmol) of bis(methylene)digermacyclohexane **6b** and 2.56 g (7.85 mmol) of GeI$_2$ in 25 ml benzene was stirred and heated gently for 0.5 h. After filtration of the solution under argon and removal of the solvent, a clear crystalline yellow residue was obtained, from which 3.0 g (4.9 mmol) of pure diiodide **9g** was recrystallized from a benzene/hexane (3.5/2.3) mixture; m.p. 101–102°C. $^1$H NMR spectrum (80 MHz, CDCl$_3$): $\delta$ (ppm): 0.29 (s, 12H, CH$_3$); 1.71 (t, 4H, $CH_2$GeMe, $J = 0.7$ Hz); 2.98 (t, 4H, CH$_2$GeI$_2$, $J = 0.7$ Hz). After alkylation with an excess of methylmagnesium iodide at $-80$°C and the usual treatment, 1.63 g (4.2 mmol) of crude **9b** was isolated. By sublimation (70–80°C/0.05 mmHg) pure **9b** was obtained as colourless crystals melting at 35°C (76.1%). $^1$H NMR spectrum (80 MHz, CDCl$_3$, $\delta$ ppm): 0.22 (s, 12H, Me$_2$Ge-GeMe$_2$); 0.25 (s, 6H, Me$_2$Ge); 1.60 (broad s, 4H, CH$_2$Ge–GeCH$_2$); 1.65 (broad s, 4H, CH$_2$–Ge–CH$_2$). IR spectrum: $\nu$(C=C) 1602w cm$^{-1}$. Mass spectrum (70 eV, $m/e$, rel. int.): 388, 40, ($M^+$); 373, 12, $(M-\mathrm{CH_3})^+$; 271, 7, $(\mathrm{Me_6Ge_2})^+$; 206, 74, $(\mathrm{Me_4Ge_2})^+$; 167, 6; 119, 100, $(\mathrm{Me_3Ge})^+$; 104, 7, $(\mathrm{Me_2Ge})^+$; 89, 33, $(\mathrm{MeGe})^+$.

This compound oxidizes slowly at the Ge–Ge bond on contact with air at room temperature to give a viscous liquid. The mass spectrum (70 eV) gives an ion at 404 $(M+16)^+$.

### *2,3,4,5,6,7-Hexahydro-5,5,6,6-tetramethyl-2,2-diphenyl-1*H*-2,5,6-trigermaindene* (**9e**)

Similarly, from **6b** (2.52 g, 5.83 mmol), GeI$_2$ (2.89 g, 8.83 mmol), and further arylation with an excess (50 mmol) of phenylmagnesium bromide in ether at $-80$°C, was obtained 1.46 g (33.8%) of pure **9e**. m.p. 110–111°C. $^1$H NMR (80 MHz, CDCl$_3$): $\delta$ (ppm): 0.25 (s, 12H, CH$_3$); 1.75 (broad s, 4H, $CH_2$GeMe); 2.11 (broad s, 4H, $CH_2$GeMe); 2.11 (broad s, 4H, CH$_2$GePh); 7.28 to 7.51 (m, 10H, C$_6$H$_5$). Mass spectrum (70 eV, $m/e$, rel. int.): 512, (6) ($M^+$); 308 (23) $(M-\mathrm{C_{11}H_{15}Ge_2})^+$; 151 (100), $(\mathrm{C_6H_5Ge})^+$; 99, (11), $(\mathrm{GeC_2H})^+$.

### *Synthesis of digermane* **10b**

A mixture of bis(methylene)diphenylgermacyclopentane (**3d**) (4.79 g, 15.6 mmol) germanium diiodide (4.90 g, 15.6 mmol), and 50 ml of benzene was heated under reflux until germanium diiodide was consumed (1 h). After removal of the solvent, the diiodide **2j** was isolated in almost quantitative yield as yellow crystals melting at 164°C. $^1$H NMR spectrum (80 MHz, CDCl$_3$): $\delta$ (ppm): 2.07 (t, 4H, CH$_2$GePh, $J = 1.8$ Hz); 3.04 (t, 4H, CH$_2$GeI$_2$, $J = 1.8$ Hz); 7.34–7.60 (m, 10H, C$_6$H$_5$). Anal. Found: C, 34.22; H, 2.86. C$_{18}$H$_{18}$GeI$_2$ calc.: C, 34.14; H, 2.86%. This diiodide, dissolved in 6.24 g (15.6 mmol) of tetrabromide **1** and 50 ml THF, was rapidly added to a suspension of activated zinc powder in 10 ml THF. After heating under reflux for 2 h and the usual treatment, 3.05 g of crude product were obtained. Chromatography on silica gel gave 1.66 g (3.6 mmol) of pure **10b** (23.1%). m.p. 79–80°C. IR spectrum (KBr): $\nu$ (cm$^{-1}$): 3065 (=CH$_2$); 1620, 1594 (C=C). $^1$H NMR (80 MHz, CDCl$_3$, $\delta$ ppm): 1.77 (m, 4H, PhGeC-C-CH$_2$GeC); 1.99 (t, 8H, Ge$CH_2$-C = CH$_2$, CH$_2$GePh); 4.77 (q, 2H, CH$_2$=C); 5.17 (q, 2H, CH$_2$=C); 7.30–7.57 (m, 10H, C$_6$H$_5$). Anal. Found: C, 62.49; H, 5.51. C$_{24}$H$_{26}$Ge$_2$ calc.: C, 62.71; H, 5.70%.

### *Synthesis of trigermane* ***12b***

To 1.29 g (2.8 mmol) of digermane **10b** was added 0.95 g (2.9 mmol) of germanium diiodide and 30 ml of benzene and the mixture was boiled for 2 h. After removal of the excess (0.03 g) $GeI_2$ and the solvent, the crude spirodiiodide **11b** (2.21 g) was obtained in quantitative yield as a yellow glassy solid. $^1H$ NMR spectrum (80 MHz, $CDCl_3$) $\delta$ (ppm): 1.58 (m, 4H, $GeCH_2$-C-$CGeI_2$); 1.72 (m, 4H, $GeCH_2$-C-CGePh); 1.98 (m, 4H, $CH_2GePh$); 2.79 (m, 4H, $CH_2GeI_2$); 7.31–7.58 (m, 10H, $C_6H_5$). Reduction of a mixture of **11b** (2.8 mmol) and tetrabromide **1** (1.50 g, 3.75 mmol) with zinc dust in 10 ml THF gave, after the usual treatment, 1.3 g of residue. Purification over silica gel (eluent pentane + 2% diethyl ether) gave 0.60 g of pure bis(methylene)trigermane **12b** (35.0%) as white crystals melting at 166°C. IR spectrum ($CDCl_3$, $\nu$ $cm^{-1}$): 3071 (=$CH_2$); 1631, 1620, 1614, 1594 (C=C). $^1H$ NMR spectrum (80 MHz, $CDCl_3$): $\delta$ (ppm): 1.74 (s, 12H, $GeCH_2$-C=C-$CH_2$); 1.99 (m, 8H, PhGe-$CH_2$ + $CH_2$-C=); 4.80 and 5.20 (m, 4H, =$CH_2$); 7.31–7.58 (m, 10H, $C_6H_5$). Anal. Found: C, 59.06, H, 5.49. $C_{30}H_{34}Ge_3$ calc.: C, 58.84; H, 5.60%.

### *Synthesis of tetragermane* ***14b***

Reaction of 0.30 g (0.49 mmol) of trigermane **11b** with an excess of germanium diiodide (0.21 g) in 5 ml benzene (reflux, 1 h) gave, after removal of the solvent and unreacted $GeI_2$ (0.05 g), a quantitative yield of crude diiodide. After alkylation with a large excess of methylmagnesium iodide (0.05 mol) and the usual treatment, 0.20 g (0.05 mmol) of bispirotetragermane **14b** (57.1%) was obtained. m.p. 214°C (dec.). $^1H$ NMR spectrum (80 MHz, $CDCl_3$): $\delta$ (ppm): 0.31 (s, 6H, $CH_3$); 1.51 (m, 4H, $CH_2$-GeMe); 1.71 (br.s, 16H, PhGeC-C-$CH_2GeCH_2$-C-$CH_2GeCH_2$); 1.98 (m, 4H, $CH_2GePh$); 7.29–7.55 (m, 10H, $C_6H_5$). Mass spectrum (70 eV, $m/e$, rel. int.): 380, 38, $(M - C_{14}H_{22}Ge_2)^+$; 229, 45; 227, 57; 169, 52, $(C_7H_8Ge)^+$; 151, 100, $(C_6H_5Ge)^+$; 89, 59, $(CH_3Ge)^+$. Anal. Found: C, 54.08; H, 5.60. $C_{32}H_{40}Ge_4$ calc.: C, 53.75; H, 5.64%.

### *Synthesis of the silagermane* ***10a***

Reaction of germanium diiodide (4.62 g, 14.1 mmol) with an equimolecular amount (3.71 g) of bis(methylene)diphenylsilacyclopentane **3c** in boiling benzene (0.5 h) gave a nearly quantitative yield of the bicyclic diiodide **2i** as orange crystals. $^1H$ NMR spectrum (80 MHz, $CDCl_3$): $\delta$ (ppm): 1.94, (t, 4H, $CH_2Si$, $J = 2$ Hz); 3.02 (t, 4H, $CH_2Ge$, $J = 2$ Hz); 7.33–7.55 (m, 10H, $C_6H_5$). Reaction of **2i** (8.33 g, 14.1 mmol) and tetrabromide **1** (9.0 g, 22.5 mmol) with an excess of activated zinc powder in boiling THF led to 6 g of residue which, after purification by chromatography on silica gel (eluent pentane), was pure **10a**, 4.20 g (71.7%) a colourless viscous liquid, $n_D^{20} = 1.6164$; IR spectrum (KBr): $\nu$ ($cm^{-1}$): 3067, 3047 (=$CH_2$); 1624, 1612, 1588 (C=C). $^1H$ NMR spectrum (80 MHz, $CDCl_3$): $\delta$ (ppm): 1.83 (m, 4H, Ge$CH_2$-C-$CH_2Si$); 1.89 (m, 4H, $CH_2Si$); 2.04 (t, 4H, Ge$CH_2$-C=$CH_2$); 4.81 (q, 2H, $CH_2$=C); 5.22 (q, 2H, $CH_2$=C); 7.35–7.63 (m, 10H, $C_6H_5$). Anal. Found: C, 69.81; H, 6.46. $C_{24}H_{26}GeSi$ calc.: C, 69.44; H, 6.31%.

### *Synthesis of the siladigermane* ***12a***

Addition of germanium diiodide (1.22 g, 3.73 mmol) to the silagermane **10a** (1.55 g, 3.73 mmol) in 5 ml benzene gave the expected cycloadduct **11a**; $^1H$ NMR spectrum (80 MHz, $CDCl_3$) $\delta$ (ppm): 1.80 (m, 12H, $SiCH_2$-C-$CH_2GeCH_2$); 2.98

(m, 4H, $CH_2GeI_2$); 7.32–7.68 (m, 10H, $C_6H_5$). Reaction of this diiodide (2.77 g, 3.73 mmol) and tetrabromide **1** (2.98 g, 7.45 mmol) with an excess of powdered zinc in 20 ml of boiling THF gave, after purification on silica gel (eluent pentane/ether (95/5)) 1.47 g (69.4%) of pure **12a**. m.p. 151°C (dec.). IR spectrum ($CDCl_3$): $\nu$ ($cm^{-1}$): 3053 (=$CH_2$); 1623, 1611, 1588 (C=C). $^1H$ NMR spectrum (80 MHz, $CDCl_3$): $\delta$ (ppm): 1.78 (br.s, 8H, $GeCH_2$-C-$CH_2Ge$); 1.84 (br.s, 4H, Si–C–C–$CH_2Ge$); 1.90 (br.s, 4H, $CH_2Si$); 2.03 (t, 4H, $GeCH_2$-C=$CH_2$); 4.82 (q, 2H, $CH_2$=C); 5.23 (q, 2H, $CH_2$=C); 7.35–7.68 (m, 10H, $C_6H_5$). Anal. Found: C, 63.80; H, 6.24. $C_{30}H_{34}Ge_2Si$ calc.: C, 63.45; H, 6.03%.

*Synthesis of the trigermane 15*

Cycloaddition of germanium diiodide (2.02 g, 6.19 mmol) to tetrakis(methylene) spirogermane (**7b**) (0.72 g, 3.09 mmol) gave the expected tetraoidide. $^1H$ NMR spectrum (80 MHz, $CDCl_3$): $\delta$ (ppm): 1.78 (m, 8H, $CH_2GeCH_2$); 2.96 (m, 8H, $CH_2GeI_2$). Further reaction with tetrabromide **1** (4.9 g, 12.25 mmol) and activated zinc (5 g) in 60 ml boiling THF gave after the usual treatment and purification by liquid chromatography (eluent pentane/ether (98/2)) 0.31 g (18.6 yield) of pure **15**, m.p. 196°C (dec.). IR spectrum ($CDCl_3$): $\nu$ ($cm^{-1}$): 3071 (=$CH_2$); 1624, 1612 (C=C). $^1H$ NMR spectrum (80 MHz, $CDCl_3$): $\delta$ (ppm): 1.70 (s, 16H, $GeCH_2CCH_2GeCH_2CCH_2Ge$); 1.96 (t, 8H, $GeCH_2C$=$CH_2$); 4.75 (q, 4H, C=$CH_2$); 5.16 (q, 4H, C=$CH_2$). Mass spectrum (70 eV, $m/e$, rel. int.): 538, 14 ($M^+$); 306, 100 $(M - C_{12}H_{16}Ge)^+$; 158, 68 $(M - C_{18}H_{25}Ge_2)^+$.

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