

Organogermanium dendrimers ¹

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Abstract

The first organogermanium dendrimers were synthesized by using divergent and convergent routes. The principal reactions used for these syntheses are hydrogermylation or hydrozirconation-transmetalation. These dendrimers were characterized by their IR, ¹H NMR and ¹³C NMR spectra and by the MALDI mass spectra of their adducts with suitable thioesters.

Keywords: Organogermanium; Dendrimers; Hydrogermylation; Hydrozirconation; Synthesis

1. Introduction

Numerous dendrimers (i.e. oligomers having a branched structure) have been described in recent years [1a–d]. In the field of organometallic chemistry of Group 14 elements, only organosilicon dendrimers (having the siloxane or carbosilane structures) have been synthesized by divergent [2–11] or convergent [12] methods. Although some organogermanium star-branched polymers have been prepared [13], no synthesis of dendrimers based on germanium atoms has yet been described.

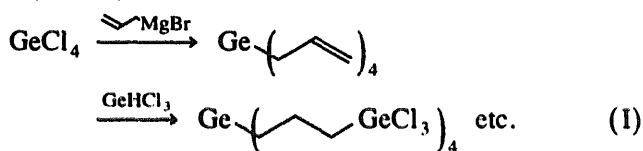
2. Results and discussion

We describe here the synthesis of organogermanium dendrimers by using divergent and convergent methods.

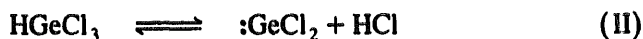
2.1. Divergent method (Scheme 1, (a))

At first appearance, the simplest method of preparation consists of successive alkenylations (using allyl- or

vinylmagnesium bromide) and hydrogermylations, starting with germanium tetrachloride (I)



Contrary to hydrosilylation of ethylenic organosilanes which requires a catalyst (H₂PtCl₆), hydrogermylation of ethylenic organogermanes occurs rapidly and exothermally in the absence of a catalyst. Trichlorogermane, however, which is much less stable than trichlorosilane, is in equilibrium with dichlorogermylene (II)



and, prepared by the reaction of hydrogen chloride with a mixture of powdered germanium and copper at 450°C [14], it also contains an appreciable amount of germanium tetrachloride which is difficult to separate.

With allylic derivatives of germanium (and the vinylic derivatives to a lesser extent) being very sensitive to electrophilic reagents [15], cleavage of germanium–carbon bonds occurs simultaneously with the addition

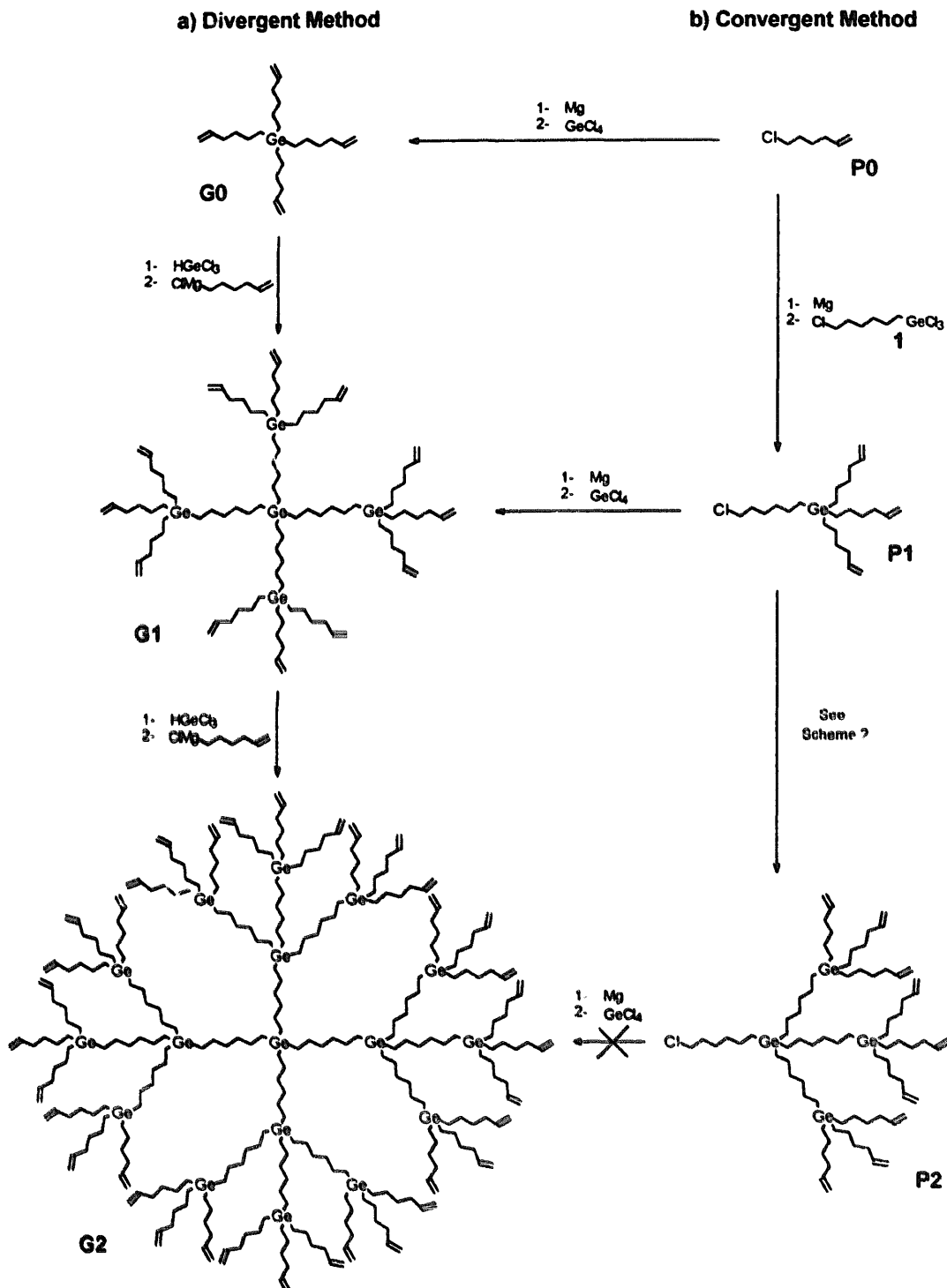
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¹ Dedicated to Professor Robert Corriu in recognition of his outstanding contributions to organosilicon chemistry.

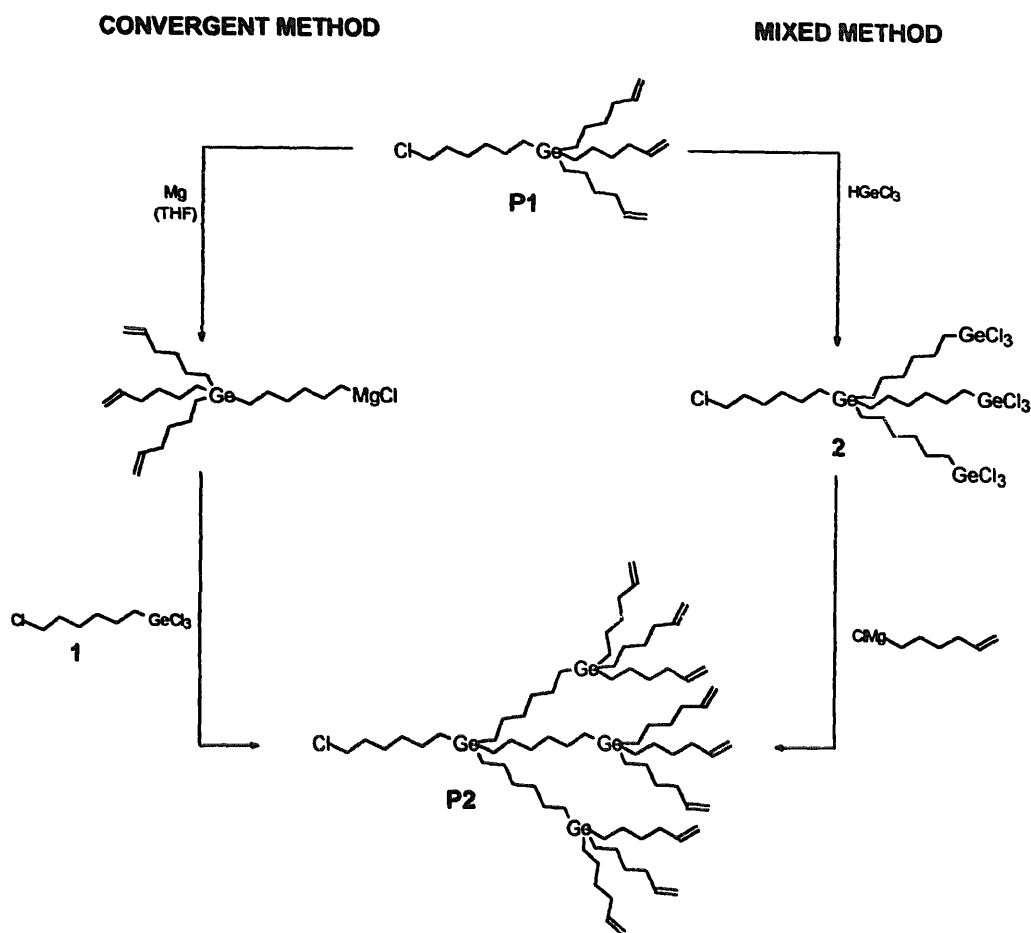
reaction, forming undesirable by-products which are difficult to remove.

To avoid these difficulties and to diminish the steric strain resulting from the accumulation of branched chains, we have used six-membered ω -ethylenic chains which are more stable chemically than α - and β -ethyl-

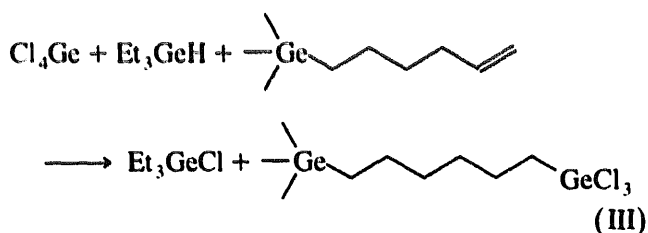
enic chains. Moreover, the trichlorogermane, free of hydrogen chloride, was prepared in situ by reduction of germanium tetrachloride in the absence of solvent (the reduction of germanium tetrachloride in the presence of ether [16] produces the etherate of germanium dichloride [17]). Reduction using $(\text{HMe}_2\text{Si})_2\text{O}$ [18] proceeds



Scheme 1. Synthesis of **G0**, **G1** and **G2** by divergent and convergent methods.



too slowly, whereas reduction by triethylgermane (III) is complete within a few hours at ambient temperature.

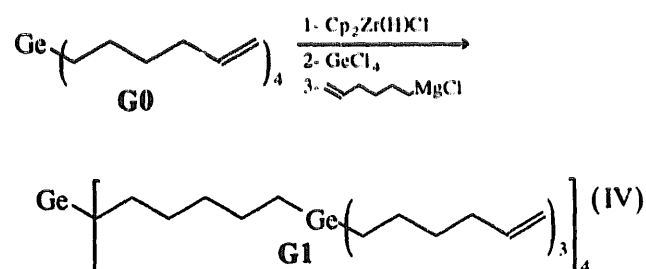


Under the experimental conditions used (ambient temperature, absence of solvent and catalyst), triethylgermane does not add to the unsaturation. The slow step is the reduction of germanium tetrachloride; the trichlorogermane which is formed then adds rapidly to the ethylenic derivatives.

This method allowed us to prepare the second generation **G2** of the alkyl germanium dendrimers having a molecular weight of 5590 u.m.

We also tried to prepare organogermanium dendrimers of this type by hydrozirconation of organoger-

manium polyalkenes, followed by transmetalation and alkenylation (IV)



However, the dendrimer **G1** thus obtained was contaminated with a series of by-products and, therefore, the direct hydrogermylation seems more advisable.

2.2. Convergent method (Scheme 1, (b))

Another possibility for obtaining this type of dendrimer consists of condensing on a germanium atom a

system of chains already branched. In this case, the starting material is the 6-chloro-1-hexene.

Direct hydrogermylation of this derivative is not univocal [19]; moreover, 6-trichlorogermyl-1-chlorohexane is obtained in only low yield (ca. 20%) when the three reagents are mixed at ambient temperature, as well as by the addition of 6-chlorohexene to germanium tetrachloride previously reduced by triethylgermane at 20°C. In contrast, by addition of triethylgermane to a mixture of 6-chlorohexene and excess germanium tetrachloride heated to 50°C, the more rapid reaction gives the expected derivative in 54% yield.

Finally, a 73% yield was obtained by addition of an equimolar mixture of triethylgermane and 6-chlorohexene to an excess of germanium tetrachloride at 50°C.

Alkylation of this derivative, followed by condensation of the corresponding organomagnesium with germanium tetrachloride, gives dendrimer **G1** identical to that obtained by the divergent method.

The precursor **P2** was obtained by the two following methods (Scheme 2):

— alkylation of trichloro derivative **1** by the organogermanium derivative of **P1**. This method is slow and the derivative **P2** was isolated in only poor yield;

— hydrogermylation of precursor **P1** followed by alkylation of product **2** formed by the Grignard reagent of 6-chlorohexene.

The synthesis of dendrimer **G2** by the convergent

route starting from precursor **P2** could not be achieved, probably because of steric constraints.

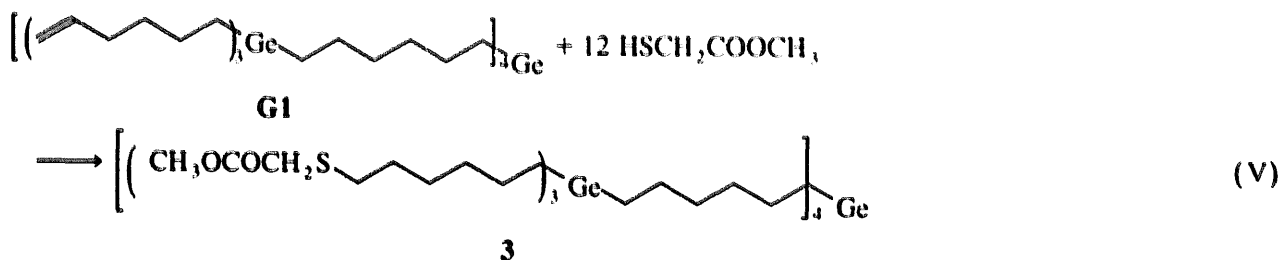
2.3. Purification and characterization

The difficulties encountered during the course of this work were of two types.

Firstly, in these reactions small quantities of impurities are formed that are often very difficult to eliminate. Chromatography on pure silica proved to be insufficient (notably for the purification of **G1**), and to obtain pure dendrimers we had to use silica impregnated with appropriate metal salts. The separation is a little improved when one uses cobalt chloride, while with copper chloride the products are too firmly retained. The best results were obtained by using nickel chloride.

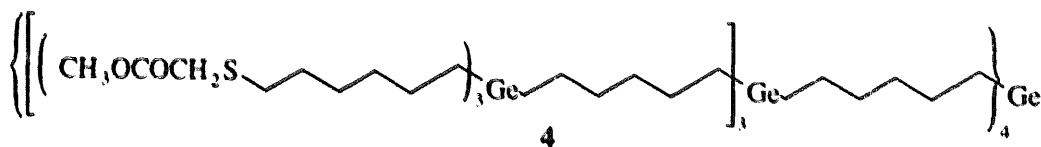
Secondly, the characterization of these molecules is difficult; IR and NMR spectra of the different molecules are very similar, and mass spectra are difficult to obtain. Although the mass spectrum of dendrimer **G0** was easily obtained by electron impact, the higher homologs **G1** and **G2** could not be characterized by the usual methods (IE, FAB, etc.).

With the object of characterizing such compounds by MALDI spectroscopy [20], we succeeded in functionalizing these dendrimers by means of methyl thioglycolate which gives a rapid and quantitative addition reaction with unsaturations (V)



The spectrum of compound **3**, obtained with a matrix derived from cinnamic acid, shows the expected signal, but poorly resolved, in the region corresponding to the

calculated molecular mass ($M = 2971$). Similarly, dendrimer **G2** gives quantitatively the corresponding adduct **4**



Organogermanium functional dendrimers resulting from the addition of thioglycolic acid or methylthioglycolate to dendrimers **G1** or **G2** are similar to micelles having an internal covalent structure and an external polar surface.

3. Experimental details

3.1. Transition-metal salt impregnated silicagels

Silicagel (Merck 60, 230–400 mesh) (100 g) was suspended in a solution of nickel chloride hexahydrate (15 g) in 1500 ml water. The resulting suspension was filtered on no. 3 sintered glass and then dried in an oven at 140°C with occasional stirring to obtain a homogeneous yellow fluid powder (10 h). The product was stored in a tightly-closed vessel. Similarly, from cobaltous and cupric chlorides were obtained the corresponding blue (Co) and yellow (Cu) impregnated silicagel.

3.2. $Cl_3Ge(CH_2)_6Cl$ (**1**)

First preparation. Triethylgermane (16.14 g, 0.100 mol) and germanium tetrachloride (40.00 g, 0.186 mol) were mixed together at room temperature. 8 h later, triethylgermane was entirely consumed and 6-chloro-1-hexene (11.50 g, 0.097 mol) was added under stirring. After completion of the reaction (12 h), the mixture was distilled giving 5.30 g (18% yield) of pure **1**. B.p. 106–107°C/0.15 mmHg; $n_D^{20} = 1.4995$. Ref. [17] 16% yield, B.p. 89–91°C/0.20 mmHg.

1H NMR (80 MHz, $CDCl_3$): $\delta = 3.52$ (t, $^3J(H,H) = 6.3$ Hz, 2H; CH_2Cl), 2.35–1.05 (m, 10H; CH_2) ppm.

Second preparation. Triethylgermane (14.98 g, 0.093 mol), germanium tetrachloride (38.00 g, 0.177 mol) and 6-chloro-1-hexene (10.70 g, 0.090 mol) were mixed together at room temperature. After completion of the reaction (3 days), distillation of the mixture gave 6.32 g of pure **1** (23% yield).

Third preparation. To a mixture of 6-chloro-1-hexene (5.93 g, 0.050 mol) and germanium tetrachloride heated at 50°C was dropwise added 8.04 g (0.050 mol) of triethylgermane. At the end of the reaction (1 h), distillation of the mixture gave 8.06 g of pure **1**. B.p. 108–109°C/0.4 mmHg (54% yield).

Fourth preparation. An equimolar mixture of 6-chloro-1-hexene (5.93 g, 0.050 mol) and triethylgermane (8.04 g, 0.050 mol) was added to germanium tetrachloride (21.44 g, 0.100 mol) heated at 50°C. After completion of the reaction (30 min), distillation of the mixture gave 10.90 g of pure **1**. B.p. 115–116°C/0.6 mmHg (73% yield).

3.3. $[CH_2=CH-(CH_2)_4]_3Ge(CH_2)_6Cl$ (**P1**)

Alkylation of 10.63 g (0.035 mol) of **1** with the Grignard reagent obtained from 23.53 g (0.198 mol) of 6-chloro-1-hexene in THF gave, after usual treatment, 15.55 g (99% yield) of nearly pure **P1**. A purified sample over silicagel (eluent pentane) showed the following physical properties.

$n_D^{20} = 1.4861$. Anal. Found: C, 65.26; H, 10.37. $C_{24}H_{45}ClGe$. Calc.: C, 65.27; H, 10.27%. IR ($CDCl_3$ soln.): $\nu = 3074.8$ (=C–H), 2922.8, 2853.0, 1820.2, 1640.4 (C=C), 1451.4, 1346.7, 1300.2, 1160.3, 996.2, 909.3, 691.6, 653.8 cm^{-1} .

1HNMR (80 MHz, $CDCl_3$): $\delta = 6.12$ –5.50 (m, 3H; –CH=), 5.28–4.70 (m, 6H; = CH_2), 3.54 (t, $^3J(H,H) = 6.5$ Hz, 2H; CH_2Cl), 2.55–1.75 (m, 6H; CH_2 –CH=), 1.75–1.05 (m, 20H; CH_2), 1.00–0.42 (m, 8H; CH_2Ge) ppm.

$^{13}CNMR$ (50 MHz, attached proton test, $CDCl_3$): $\delta = 139.1$ (CH=), 114.2 (= CH_2), 45.1 (CH_2Cl), 33.5–25.1 (CH_2), 24.7 (CH_2 –CH=), 12.7–12.5 (CH_2Ge) ppm. Total absence of signals corresponding to CH_3 and saturated CH carbons.

3.4. $\{[CH_2=CH-(CH_2)_4]_3Ge(CH_2)_6\}_3Ge(CH_2)_6Cl$ (**P2**)

Convergent method. Alkylation of 2.99 g (0.010 mol) of **1** with the Grignard reagent obtained from 20.67 g (0.047 mol) of **P1** in THF gave, after usual treatment, 0.98 g (7% yield) of nearly pure **P2**. A purified sample over silicagel (eluent pentane) had the following physical properties.

Anal. Found: C, 65.98; H, 10.54. $C_{78}H_{147}ClGe_4$. Calc.: C, 66.40; H, 10.50%.

1HNMR (80 MHz, $CDCl_3$): $\delta = 6.07$ –5.70 (m, 9H; CH=), 5.15–4.74 (m, 18H; CH_2 =), 3.54 (t, $^3J(H,H) = 6.5$ Hz, 2H; CH_2Cl), 2.24–1.72 (m, 18H; CH_2 –CH=), 1.72–1.03 (m, 68H; CH_2), 1.03–0.44 (m, 32H; CH_2Ge) ppm.

^{13}CMR (50MHz, attached proton test, $CDCl_3$): $\delta = 139.1$ (CH=), 114.2 (= CH_2), 45.2 (CH_2Cl), 33.4–25.2 (CH_2), 24.7 (CH_2 –CH=), 12.8–12.5 (CH_2Ge) ppm. Total absence of signals corresponding to CH_3 and saturated CH carbons.

Mixed method. Trichlorogermane (5.0 g, 0.027 mol) and **P1** (2.84 g, 0.006 mol) were mixed together at room temperature. After completion of the reaction (1 h), distillation of the mixture gave 5.75 g of pure **2** (97%). Alkylation of 5.75 g (0.006 mol) of **2** with the Grignard reagent obtained from 11.90 g (0.100 mol) of 6-chloro-1-hexene in THF gave, after usual treatment and purification over silicagel (eluent pentane), 2.80 g (34% yield) of pure **P2** having exactly the same physi-

cal properties as the compound prepared by the convergent method.

3.5. G0

A solution of hexenylmagnesium chloride was prepared by reaction of 23.01 g (0.194 mol) of 6-chlorohexene with an excess of magnesium turnings (10.0 g, 0.411 mol) in 150 ml of dry ether (the reaction must be initiated with 1.0 g, 5.3 mmol, of 1,2-dibromoethane). At the end of the addition, the mixture was boiled for 1 h, then cooled. The Grignard reagent solution was decanted from the unreacted magnesium and poured in a 1 l flask; 500 ml of ether was added and a solution of germanium tetrachloride (6.50 g, 30.3 mmol) in 250 ml ether was then added dropwise under magnetic stirring. A pasty-white precipitate was formed progressively. The resulting mixture was boiled for 5 h, then cooled in ice; the excess of Grignard reagent was hydrolyzed and the organic phase extracted and dried over sodium sulfate. After removal of the solvent, the residue (10.65 g, 86.8% yield) was dissolved in 400 ml pentane and the solution filtered through 50 g of silicagel. Evaporation of the filtrate gave 9.61 g (78.3% yield) of nearly pure tetrahexenylgermane. Chromatographically pure product was obtained by chromatography of 1.0 g of compound on 45 g Ni-impregnated silicagel (eluent pentane).

Anal. Found: C, 71.44; H, 11.11. $C_{24}H_{44}Ge$. Calc.: C, 71.14; H, 10.95%.

IR (neat): $\nu = 3075.9$ ($=C-H$), 2995.9, 2976.0, 2922.9, 2851.4, 1821.1, 1640.6 ($C=C$), 1458.6, 1445.6, 1416.2, 1346.8, 1301.4, 1248.3, 1159.8, 1059.4, 993.3, 908.8, 693.7, 624.8 cm^{-1} .

1H NMR (80 MHz, $CDCl_3$): $\delta = 6.11-5.54$ (m, 4H; $CH=$), 5.15–4.76 (m, 8H, $CH_2=$), 2.51–1.76 (m, 8H; $CH_2-CH=$), 1.76–1.06 (m, 16 H; CH_2), 1.06–0.44 (m, 8H; CH_2Ge) ppm.

^{13}C NMR (50 MHz, attached proton test, $CDCl_3$): $\delta = 139.1$ ($CH=$), 114.1 ($=CH_2$), 33.5–32.8 ($CH=CH_2-CH_2-$), 24.7 (CH_2), 12.5 (CH_2Ge) ppm. Total absence of signals corresponding to CH_3 and saturated CH carbons.

MS (70eV) (^{74}Ge) m/e (I_{rel}): 405 (1, $M - 1$)⁺; 323 (21, $M - C_6H_{11}$)⁺; 241 (27, $M - 2C_6H_{11}$)⁺; 159 (54, GeC_6H_{11})⁺; 129(16); 89 (15, $GeCH_3$)⁺; 81 (23, C_6H_9)⁺; 55 (100, C_4H_7)⁺.

3.6. G1

3.6.1. Divergent route

A mixture of tetrahexenylgermane (1.01 g, 2.5 mmol), triethylgermane (1.61 g, 10 mmol) and germanium tetrachloride (2.14 g, 10 mmol) was stirred under argon at

room temperature and the reaction was monitored by NMR. After 3 days, the 1H NMR spectrum of the mixture showed the vanishing of signals corresponding to both ethylenic and Ge-H protons. Triethylgermane chloride formed was eliminated by heating the mixture under vacuum (b.p. 60–62°C/13 mmHg, 1.83 g, 94% yield). The residue (2.44 g, 2.17 mmol, 87% yield) was dissolved in 25 ml THF and added dropwise to an excess of hexenylmagnesium chloride (50 mmol). The mixture was boiled for 5 h and after usual treatment, 3.52 g of crude G1 was obtained (83% yield). Repeated purifications on Ni-impregnated silica (1 g G1, 30 g silicagel, eluent pentane) gave chromatographically pure G1 having the following physical properties.

IR ($CDCl_3$ soln.): $\nu = 3076.7$ ($=C-H$), 2975.8, 2918.4, 2851.6, 1639.3 ($C=C$), 1459.5, 1418.0, 1383.2, 1345.6, 1301.3, 1259.5, 1097.8, 1001.1, 917.7, 749.5, 738.5, 728.2, 695.0, 652.0 cm^{-1} .

1H NMR (80 MHz, $CDCl_3$): $\delta = 6.14-5.52$ (m, 12H; $CH=$), 5.20–4.80 (m, 24H; $CH_2=$), 2.40–1.78 (m, 24H; $CH_2-CH=$), 1.78–1.00 (m, 80H; CH_2), 1.00–0.35 (m, 40H; CH_2Ge) ppm.

^{13}C NMR (50 MHz, attached proton test, $CDCl_3$): $\delta = 139.1$ ($CH=$), 114.2 ($CH_2=$), 33.5–32.8 ($CH=CH_2-CH_2-$), 25.3–24.7 (CH_2), 12.8–12.6 (CH_2Ge) ppm. Total absence of signals corresponding to CH_3 and saturated CH carbons.

3.6.2. Convergent route

A Grignard reagent was prepared by reaction of pure PI (14.31 g, 0.032 mol) with magnesium turnings (6.00 g, 0.25 mol) in 125 ml THF (the reaction was initiated with 0.94 g, 5.0 mmol of 1,2-dibromoethane). After 10 h boiling, the unreacted magnesium was separated and to the filtrate was added a solution of germanium tetrachloride (1.29 g, 6.0 mmol) in 30 ml THF and the resulting mixture boiled for 2 h. After usual treatment, 11.5 g of crude G1 was obtained. Repeated purifications on Ni-impregnated silicagel (30 g each, eluent pentane) gave 2.90 g (1.7 mmol) of pure G1 (28% yield) identical to G1 samples obtained by other routes.

3.6.3. Synthesis of G1 by hydrozirconation

A mixture of G0 (1.01 g, 2.5 mmol) and bis(cyclopentadienyl)zirconium chloride hydride [21] (2.60 g, 10 mmol) in 10 ml THF was stirred under argon at room temperature. The mixture, initially clear yellow, turned dark red within 3 h. This solution was added dropwise to a large excess (10.72 g, 50 mmol) of $GeCl_4$ in 100 ml ether, and the clear yellow suspension was stirred 10 h at 20°C then boiled for 2 h. After removal of the excess of $GeCl_4$ by distillation and Cp_2ZrCl_2 by filtration, this ether-pentane solution was treated with an excess of hexenylmagnesium chloride in THF. After

usual treatment was obtained 3.57 g of residue containing **G1** and several unidentified products. **G1** was isolated by chromatography on Ni-impregnated silicagel and was found identical (R_f , IR and NMR spectra) to **G1** samples prepared by other routes.

3.7. **G2**

3.7.1. Divergent route

A mixture of pure **G1** (0.70 g, 0.412 mmol), triethylgermane (0.84 g, 5.22 mmol) and germanium tetrachloride (2.00 g, 9.32 mmol) was stirred up to the vanishing of the signals corresponding to ethylenic protons in the NMR spectrum of the mixture (17 days). Removal of the excess of germanium tetrachloride and triethylgermanium chloride gave a white solid residue (0.92 g). The solid was dissolved in 50 ml THF and treated with an excess (0.05 mol) of hexenylmagnesium chloride in the same solvent. After usual treatment, a pasty liquid, crude **G2**, was obtained (1.09 g, 82% yield). Careful purification on silicagel (eluent pentane + 20% CCl_4) gave chromatographically pure **G2** having the following physical properties.

IR (CDCl_3 soln.): $\nu = 3076.7$ (=C–H), 2975.9, 2924.4, 2851.3, 1639.2 (C=C), 1459.4, 1417.8, 1347.9, 1125.6, 1000.3 cm^{-1} .

^1H NMR (80 MHz, CDCl_3): $\delta = 6.10$ – 5.48 (m, 36H; CH=), 5.26–4.70 (m, 72H, CH_2 =), 2.38–1.78 (m, 72H; CH_2 –CH=), 1.78–1.00 (m, 272H; CH_2), 1.00–0.24 (m, 136H, CH_3Ge) ppm.

^{13}C NMR (50 MHz, attached proton test, CDCl_3): $\delta = 139.1$ (CH=), 114.2 (CH_2 =), 33.5–32.8 ($\text{CH}=\text{CH}_2$ – CH_2 –), 25.3–24.7 (CH_2), 12.8–12.6 (CH_3Ge) ppm. Total absence of signals corresponding to CH_3 and saturated CH carbons.

3.7.2. Convergent route (attempt)

In a carefully-dried flask, filled with argon, was placed 1.02 g (42.5 mmol) of magnesium turnings and 5 ml THF. 1,2-dibromoethane (0.94 g, 5 mmol) was added, then, at the end of the reaction, pure **P2** (2.22 g, 1.57 mmol) in 20 ml THF. The mixture was boiled for 3 days. To the filtered solution was added germanium tetrachloride (0.072 g, 0.36 mmol) and the mixture boiled for 5 h. After usual treatment, 2.09 g of clear yellow residue was obtained, containing mainly unreacted **P2**. The formation of **G2** was not detected.

3.8. $\{[\text{CH}_3\text{OCOCH}_2\text{S}-(\text{CH}_2)_6-]_3\text{Ge}-(\text{CH}_2)_6-]_4\text{Ge}$ (**3**)

To the dendrimer **G1** is added without solvent an excess (20%) of methyl thioglycolate. After completion of the reaction (30 min, 60°C), the compounds are separated over silicagel. The methyl thioglycolate is eliminated first by elution with ether–pentane (50:50)

and the derivative **3** is isolated pure by elution with ether–pentane (80:20); viscous liquid.

^1H NMR (80 MHz, CDCl_3): $\delta = 3.72$ (s, 36H; CH_3), 3.20 (s, 24H; CH_2 –CO–), 2.61 (t, $^3J(\text{H,H}) = 7.16$ Hz, 24H; CH_2 –S), 1.80–1.05 (m, 220H; CH_2), 0.85–0.42 (m, 40H; $\text{Ge}-\text{CH}_2$) ppm.

^{13}C NMR (50 MHz, attached proton test, CDCl_3): $\delta = 171.0$ (–CO–), 96.1 (– CH_2 –CO–), 52.0 (CH_3), 33.5–25.1 (CH_2), 12.9–12.6 (GeCH_2) ppm.

3.9. $\{[\text{CH}_3\text{OCOCH}_2\text{S}-(\text{CH}_2)_6-]_3\text{Ge}-(\text{CH}_2)_6-]_4\text{Ge}-(\text{CH}_2)_6-]_4\text{Ge}$ (**4**)

Similarly, the derivative **4** is obtained quantitatively by reaction between **G2** and an excess (20%) of methyl thioglycolate.

^1H NMR (80 MHz, CDCl_3): $\delta = 3.71$ (s, 108H; CH_3), 3.20 (s, 72H; CH_2 –CO), 2.61 (t, $^3J(\text{H,H}) = 7.16$ Hz, 72H; CH_2 –S), 1.80–1.05 (m, 416H; CH_2), 0.85–0.42 (m, 136H; $\text{Ge}-\text{CH}_2$) ppm.

^{13}C NMR (50 MHz, attached proton test, CDCl_3): $\delta = 171.0$ (–CO–), 96.1 (– CH_2 –CO–), 52.0 (CH_3), 33.6–21.5 (CH_2), 13.2–12.5 (GeCH_2) ppm.

References and notes

- [1] For reviews see: (a) D.D. Tomalia, A.M. Naylor and W.A. Goddard III, *Angew. Chem. Int. Ed. Engl.*, 29 (1990) 138. (b) A.B. Meckelburger, W. Jaworek and F. Vögtle, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 1571. (c) J. Issberner, R. Moors and F. Vögtle, *Angew. Chem. Int. Ed. Engl.*, 33 (1994) 2413. (d) C.J. Hawker and J.M.J. Fréchet, *J. Am. Chem. Soc.*, 112 (1990) 7638.
- [2] E.A. Rebrov, A.M. Muzafarov, V.S. Papkov and A.A. Zhdanov, *Dokl. Akad. Nauk SSSR*, 309 (2) (1989) 376.
- [3] H. Uchida, Y. Kabe, K. Yoshino, A. Kanamata, T. Tsumuraya and S. Masamune, *J. Am. Chem. Soc.*, 112 (1990) 7077.
- [4] L.J. Mathias and T.W. Carothers, *J. Am. Chem. Soc.*, 113 (1991) 4043.
- [5] A. Morikawa, M. Kakimoto and Y. Imai, *Macromolecules*, 24 (1991) 3469.
- [6] J. Roovers, P.M. Toporowski and L.L. Zhou, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, 33 (1992) 182.
- [7] A.W. van der Made and P.W.N.M. van Leeuwen, *J. Chem. Soc. Chem. Commun.*, (1992), 1400.
- [8] L.L. Zhou and J. Roovers, *Macromolecules*, 26 (1993) 963.
- [9] J. Roovers, L.L. Zhou, P.M. Toporowski, M. van der Zwan, H. Hiatrou and N. Hadjichristidis, *Macromolecules*, 26 (1993) 4324.
- [10] A.W. van der Made, P.W.N.M. van Leeuwen, J.C. de Wilde and R.A.C. Brandes, *Adv. Mater.*, (1993) 466.
- [11] D. Seyferth, D.Y. Son, A.L. Rheingold and R. Ostrander, *Organometallics*, 13 (1994) 2682.
- [12] A. Morikawa, M. Kakimoto and Y. Imai, *Macromolecules*, 25 (1992) 3247.
- [13] M.N. Bochkarev, V.B. Silkin, L.P. Maiorova, G.A. Razuraev, Yu.D. Semchikov and V.I. Sherstyanykh, *J. Organomet. Chem. USSR*, 1 (1988) 115.

- [14] A.D. Petrov, V.F. Mironov and N.G. Dzhurinskaya, *Dokl. Akad. Nauk SSSR*, 128 (1959) 302.
- [15] M. Lesbre, P. Mazerolles and J. Satgé, *The Organic Compounds of Germanium*, Wiley, New York, 1971.
- [16] M. Massol and J. Satgé, *Bull. Soc. Chim. Fr.*, 9 (1966) 2737.
- [17] O.M. Nefedov, S.P. Kolesnikov and V.I. Sheichenko, *Angew. Chem. Int. Ed. Engl.*, 3 (7) (1964) 508.
- [18] V.F. Mironov and T.K. Gar, *Zh. Obshch. Khim.*, 45 (1) (1975) 103.
- [19] R. Riemschneider, K. Menge and P. Klang, *Z. Naturforsch. Teil. B*, 11 (1956) 155.
- [20] We sincerely thank Mrs D. Promé and Miss C. Deon (Laboratoire de Pharmacologie et de Toxicologie Fondamentales, 205, route de Narbonne 31400 Toulouse) who obtained these spectra with a VG Tofspec spectrometer.
- [21] S.L. Buchwald, S.J. La Maire, R.B. Nielsen, B.T. Watson and S.M. King, *Tetrahedron Lett.*, 28 (34) (1987) 3895.