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Synthesis and Characterization of Silicon-Based Group 14 Dendrimers $Si\{(CH_2)_2Sn[(CH_2)_4MPh_3]_3\}_4$ (M = Ge, Sn)

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The catalytic hydrogermylation of $Si(CH{=}CH_2)_4$ with Ph_3GeH yielded $Si(CH_2CH_2GePh_3)_4$ (**1**). In contrast, $Sn(CH{=}CH_2)_4$ and $Sn(CH_2CH{=}CH_2)_4$ reacted with Ph_3GeH under the same conditions, forming $Ph_3Ge(CH_2)_2GePh_3$ (**2**) and $Ph_3Ge(CH_2)_3GePh_3$ (**3**), respectively, whereas the reaction of $Sn(CH_2CH_2CH{=}CH_2)_4$ and Ph_3GeH afforded the expected tin-based metallodendrimer $Sn[(CH_2)_4GePh_3]_4$ (**4**). The reactions of $Si[(CH_2)_2SnBr_3]_4$ with the Grignard reagents RMgBr (R = $CH{=}CH_2$, $CH_2CH{=}CH_2$, $(CH_2)_2CH{=}CH_2$)) produced $Si[(CH_2)_2Sn(CH{=}CH_2)_3]_4$ (**5**), $Si[(CH_2)_2Sn(CH_2CH{=}CH_2)_3]_4$ (**6**), and $Si[(CH_2)_2Sn(CH_2CH_2CH{=}CH_2)_3]_4$ (**7**). While hydrogermylation of **5** and **6** with Ph_3GeH resulted in the formation of **2** and **3**, respectively, compound **7** reacted with Ph_3GeH, providing the expected second-generation Si/Ge/Sn heterometallodendrimer $Si\{(CH_2)_2Sn[(CH_2)_4GePh_3]_3\}_4$ (**8**). Correspondingly, hydrostannylation of **7** with Ph_3SnH yielded $Si\{(CH_2)_2Sn[(CH_2)_4SnPh_3]_3\}_4$ (**9**). All compounds were characterized by multinuclear NMR studies (^1H, ^{13}C, ^{119}Sn), mass spectrometry (MALDI-TOF, EI), and elemental analyses.

Introduction

In the past decade, dendrimers attracted enormous attention due to their unique chemical properties arising from their special and well-defined architecture[1] and their potential application in catalysis,[2] medicine,[3] material sciences,[4] or host guest chemistry.[5] Metallodendrimers[6] represent a new class of dendrimers in which metal ions or metal complexes either are connected to outer functional groups of the pure organic dendrimer, thus forming the surface of the basic framework, or, in favorable cases, are part of the interior of the dendrimer. Within a short time, metallodendrimers took over an important role in the development of quite new materials useful in electro-, photo-, and magnetochemistry. In contrast to the preparation of pure organic dendrimers—the majority of which were obtained by the basic divergent or convergent route—the synthesis of metallodendrimers, especially of those containing covalently bonded metal-carbon moieties, suffers from limitations in suitable reagents and synthetic methods. Although several methods for the preparation of transition metal containing dendrimers have been described in the literature,[7] only few reports concerning the synthesis of main group metal based dendrimers are known so far.[8]

A further challenge was the synthesis of heterometallic dendrimers, which were suggested to improve specific chemical and physical properties of the homometallic dendrimers.[9] However, preparative methods for the synthesis of metallodendrimers containing different metals, in particular main group metals, are hardly developed.[10] The only examples reported up to now are silicon-based dendrimers with alternating direct bonded silicon and germanium atoms[11] as well as peripherally substituted carbosilane dendrimers containing lithium and organotin fragments.[12]

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Recently, we succeeded in the sythesis of the tin analogues[13] of the organosilicon[7e,14] and organogermanium[8c,d,g,h] dendrimers already known. In the meantime, we developed a method to synthesize the first *all*-tin dendrimer by the divergent[15] as well as by the convergent[16] route and consequently prepared a series of novel tin-based dendrimers.[17] In this paper we describe a simple method for the synthesis of hybrid metallodendrimers of group 14 elements, resulting in the isolation of the first Si/Ge/Sn heterotrimetallic dendrimer.

Experimental Section

General Comments. All manipulations involving air-sensitive compounds were carried out in dry, oxygen-free solvents and under an inert atmosphere of nitrogen using standard Schlenk techniques. Melting points were measured in sealed capillaries with a Büchi 510 melting point determination apparatus and are uncorrected. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O analyzer 2400. The NMR spectra were recorded on Bruker ARX 200 (^1H, 200.13 MHz; ^{13}C, 50.32 MHz) and ARX 400 (^1H, 400.13 MHz; ^{13}C, 100.64 MHz; ^{119}Sn, 149.21 MHz) spectrometers at ambient temperature. Chemical shifts are reported in ppm and referenced to the ^1H and ^{13}C residues of the deuterated solvents (^1H and ^{13}C) and to $(CH_3)_4Sn$ (^{119}Sn), respectively. IR spectra were obtained by using a Nicolet Magna System 750 spectrometer. Mass spectra (EI, 70 eV) were recorded on a Varian MAT 311 A/AMD instrument. Only characteristic fragments containing the isotopes of the highest abundance are listed. Relative intensities are given in parentheses.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed in the reflectron mode on an Applied Biosystems Voyager-Elite mass spectrometer equipped with a nitrogen laser emitting at 337 nm. Acceleration voltage was set to 20 and 25 kV, respectively, with positive or negative ionization. The mass spectrometer was externally calibrated with a mixture of three peptides. *trans*-Indolacrylicacid (IAA, used as purchased) served as MALDI matrix in concentrations of 0.2 and 10 mM in THF/CH_3CN (3:1), respectively. Sample solutions were prepared with an approximate concentration of 1 mM in THF or CH_2Cl_2. Solutions containing 2 mM CH_3COONa, KCl, or AgI were used as ionization agents. Sonication was applied to speed up mixing. One microliter of the sample was mixed with 1 μL of the matrix solution, and 1 μL of the resulting mixture was deposited on a stainless-steel flat plate and allowed to dry at room temperature.

$CH_2=CHBr$, $CH_2=CHCH_2Br$, $CH_2=CHCH_2CH_2Br$, Ph_3GeH, $Si(CH=CH_2)_4$, $Sn(CH=CH_2)_4$, and $Sn(CH_2CH=CH_2)_4$ were used as purchased. Ph_3SnH,[18] $Sn(CH_2CH_2CH=CH_2)_4$,[19] and $Si(CH_2CH_2SnBr_3)_4$[13a] were prepared according to published procedures.

$Si(CH_2CH_2GePh_3)_4$ (1). A stirred solution containing $Si(CH=CH_2)_4$ (0.39 g, 2.89 mmol) and 5 drops of a solution of H_2PtCl_6 (0.1 M) in isopropanol was treated with Ph_3GeH (4.40 g, 14.43 mmol) at 45 °C. After stirring the reaction mixture for 24 h at this temperature it was cooled to room temperature. The addition of pentane (25 mL) caused the precipitation of a white solid, which was separated, redissolved in toluene (5 mL), and again precipitated by adding pentane (25 mL). The precipitate was separated, washed several times with a mixture of pentane/diethyl ether (1:1), and then carefully dried in vacuum, giving **1** as white solid (3.65 g, 93%). Mp: 111 °C. ^1H NMR (400.13 MHz, $CDCl_3$): δ 0.68−0.80 (m, 8H, $SiCH_2$), 1.22−1.34 (m, 8H, $GeCH_2$), 7.28−7.40 (m, 36H, $Ph-H^{para/meta}$), 7.40−7.45 (m, 24H, $Ph-H^{ortho}$). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 4.30 ($SiCH_2$), 6.70 ($GeCH_2$), 128.18 ($Ph-C^{meta}$), 128.85 ($Ph-C^{para}$), 134.98 ($Ph-C^{ortho}$), 137.01 ($Ph-C^{ipso}$). MS MALDI-TOF (IAA, THF): 1379.80 (calcd 1379.30) $[M + Na]^+$, 1419.8 $[M + Na + K]^+$ (calcd 1418.30). Anal. Calcd for $C_{80}H_{76}Ge_4Si$ (1355.93): C, 70.87; H, 5.65. Found: C, 70.73; H, 5.57.

Attempted Hydrogermylation of $Sn(CH=CH_2)_4$. $Sn(CH=CH_2)_4$ (0.45 g, 1.98 mmol) was dropped slowly to a stirred mixture of Ph_3GeH (3.02 g, 9.92 mmol) and AIBN (0.08 g, 5 mol %, 0.50 mmol). Stirring of the reaction mixture at 45 °C for 24 h and subsequent workup as in the case of **1** afforded $Ph_3Ge(CH_2)_2GePh_3$ (**2**) as white powder (0.52 g, 0.82 mmol). ^1H NMR (400.13 MHz, $CDCl_3$): δ 1.72 (s, 4H, $GeCH_2$), 7.32−7.42 (m, 18H, $Ph-H^{para/meta}$), 7.44−7.49 (m, 12H, $Ph-H^{ortho}$). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 8.32 ($GeCH_2$), 36.80 ($Ph-C^{ipso}$), 128.23 ($Ph-C^{meta}$), 128.94 ($Ph-C^{para}$), 135.06 ($Ph-C^{ortho}$). EI MS (185 °C, *m/z* (%)): 636.2 (4) $[M]^+$, 608.1 (13.5) $[M - C_2H_4]^+$, 305.2 (100) $[HGe(C_6H_5)_3]^+$, 227.1 (8.8) $[HGe(C_6H_5)_2]^+$, 151.1 (7.8) $[HGe(C_6H_5)$. Anal. Calcd for $C_{38}H_{34}Ge_2$ (635.87): C, 71.78; H, 5.39. Found: C, 71.39; H, 5.43.

Attempted Hydrogermylation of $Sn(CH_2CH=CH_2)_4$. The reaction of $Sn(CH_2CH=CH_2)_4$ (0.38 g, 1.34 mmol), Ph_3GeH (2.05 g, 6.70 mmol), and AIBN (0.06 g, 5 mol %, 0.34 mmol) under the conditions described above afforded $Ph_3Ge(CH_2)_3GePh_3$ (**3**)[20] as a white powder (0.32 g, 0.5 mmol). EI MS (185 °C, *m/z* (%)): 650.1 (0.3) $[M]^+$, 606.9 (0.3) $[M - C_3H_6]^+$, 573.1 (0.4) $[M - C_6H_5]^+$, 531 (0.3) $[M - C_3H_6 - C_6H_5]^+$, 454 (0.3) $[M - C_3H_6 - 2C_6H_5]^+$, 377 (1.5) $[M - C_3H_6 - 3C_6H_5]^+$, 305.1 (100) $[HGe(C_6H_5)_3]^+$, 227.1 (10) $[HGe(C_6H_5)_2]^+$, 151.1 (2) $[HGe(C_6H_5)]$. Anal. Calcd for $C_{39}H_{36}Ge_2$ (649.92): C, 72.07; H, 5.58. Found: C, 78.63; H, 8.72.

$Sn[(CH_2)_4GePh_3]_4$ (4). To a stirred mixture of Ph_3GeH (3.36 g, 11.01 mmol) and AIBN (0.10 g, 5 mol %, 0.61 mmol) kept at 45 °C was added freshly distilled $Sn(CH_2CH_2CH=CH_2)_4$ (0.75 g, 2.21 mmol). Stirring of the reaction mixture for 24 h and workup in analogy with **1** afforded **4** as white solid (3.15 g, 91%). Mp: 121 °C. ^1H NMR (400.13 MHz, $CDCl_3$): δ 0.51−0.70 (m, 8H, $SnCH_2$), 1.31−1.54 (m, 24H, $SnCH_2CH_2CH_2CH_2Ge$), 7.31−7.38 (m, 36H, $Ph-H^{meta/para}$), 7.45−7.52 (m, 24H, $Ph-H^{ortho}$). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 8.43 ($SnCH_2$, $|^1J(^{13}C^{117/119}Sn)| = 296.25/310.23$ Hz), 13.66 ($SnCH_2CH_2CH_2CH_2$, $|^4J(^{13}C^{119}Sn)|$ = not detected), 29.77 ($SnCH_2CH_2CH_2$, $|^3J(^{13}C^{117/119}Sn)| = 54.84$ Hz), 30.86 ($SnCH_2CH_2$, $|^2J(^{13}C^{119}Sn)| = 19. 36$ Hz), 128.13 ($Ph-C^{meta}$), 128.79 ($Ph-C^{para}$), 134.94 ($Ph-C^{ortho}$), 137.36 ($Ph-C^{ipso}$). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −11.80. MS MALDI-TOF (IAA, THF): 1582.73 $[M + Na]^+$ (calcd 1581.82), 1406.89 $[M - 2C_6H_5]^+$. Anal. Calcd for $C_{88}H_{92}Ge_4Sn$ (1558.75): C, 67.81; H, 5.95. Found: C, 67.68; H, 5.83.

$Si[(CH_2)_2Sn(CH=CH_2)_3]_4$ (5). To a solution of $Si[(CH_2)_2SnBr_3]_4$ (4.1 g, 2.61 mmol) in THF (50 mL) was added a solution of $CH_2=CHMgBr$ in THF (47.9 mL, 0.85 M, 40.72 mmol) at 0 °C in the course of 1 h. The brown reaction mixture was stirred at 75 °C for 4 h and then at room temperature for 12 h. The resulting mixture was carefully hydrolyzed at 0 °C and filtered off from precipitated

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magnesium salt (D4-frit). The residue was extracted three times with diethyl ether (20 mL). The combined organic phases were washed once with a saturated aqueous solution of NH_4Cl (50 mL) and three times with a saturated aqueous solution of NaCl (50 mL each). Drying of the organic phase over Na_2SO_4 and subsequent evaporation of the solvents in vacuum (10^{-2} mbar) gave **5** as light yellow oil (2.21 g, 90%). IR (KBr, film): $\nu(C{=}C)$ 1639 cm^{-1} (s). ^1H NMR (200.13 MHz, $CDCl_3$): δ 0.75−1.86 (m, 16H, CH_2CH_2Sn), 5.70−5.86 (m, 24H, $Sn(CH{=}C\mathit{H}_2)_3$), 6.20−6.58 (m, 12H, $Sn(C\mathit{H}{=}CH_2)_3$). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ 2.45 ($\mathit{C}H_2CH_2Sn$, $|^2J(^{13}C^{119}Sn) = 34.61$ Hz), 6.35 (CH_2Sn, $|^1J(^{13}C^{117/119}Sn)| = 385.01/403.00$ Hz), 135.52 ($Sn(CH{=}\mathit{C}H_2)_3$, $|^2J(^{13}C^{119}Sn)|$ = not detected), 136.45, ($Sn(\mathit{C}H{=}CH_2)_3$, $|^1J(^{13}C^{117/119}Sn)| = 438.42/458.85$ Hz). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −122.75. EI MS (114 °C; *m/z* (%)): 940.7 (0.7) $[M]^+$, 482.9 (23) $[M - 2C_2H_4Sn(CH{=}CH_2)_3]^+$, 456 (6) $[M - 2C_2H_4Sn(CH{=}CH_2)_3 - CH{=}CH_2]^+$, 428.8 (3) $[M - 2CH{=}CH_2 - 2C_2H_4Sn(CH{=}CH_2)_3]^+$, 401.8 (4) $[M - 2C_2H_4Sn(CH{=}CH_2)_3 - 3CH{=}CH_2]^+$, 347.9 (4) $[M - 2C_2H_4Sn(CH{=}CH_2)_3 - 5CH{=}CH_2]^+$, 201 (100) $[C_2H_4Sn(CH{=}CH_2)_3]^+$. Anal. Calcd for $C_{32}H_{52}SiSn_4$ (939.61): C, 40.91; H, 5.58. Found: C, 40.68; H, 5.51.

$Si[(CH_2)_2Sn(CH_2CH{=}CH_2)_3]_4$ (6). To a solution of $Si[(CH_2)_2SnBr_3]_4$ (3.8 g, 2.42 mmol) in THF (50 mL) was added a solution of $CH_2{=}CHCH_2MgBr$ in THF (57.2 mL, 0.66 M, 37.75 mmol) at 0 °C. Workup similar to that used for the synthesis of **5** yielded **6** as a yellowish, viscous oil (2.12 g, 79%). IR (KBr, film): ν (C═C) 1622 cm^{-1}(s). ^1H NMR (200.13 MHz, $CDCl_3$): δ 0.64−0.97 (m, 16H, CH_2CH_2Sn), 1.84−1.96 (d, 24H, $Sn(C\mathit{H}_2CH{=}CH_2)_3$, $|^2J(^{13}H^{119}Sn)| = 61.04$ Hz), 4.60−4.93 (m, 24H, $Sn(CH_2CH{=}C\mathit{H}_2)_3$), 5.80−6.10 (m, 12H, $Sn(CH_2C\mathit{H}{=}CH_2)_3$). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ 1.67 ($CH_2\mathit{C}H_2Sn$, $|^1J(^{13}C^{117/119}Sn)| = 305.45/319.35$ Hz), 6.69 ($\mathit{C}H_2CH_2Sn$, $|^2J(^{13}C^{119}Sn)| = 34.88$ Hz), 15.97 ($Sn(\mathit{C}H_2CH{=}CH_2)_3$, $|^1J(^{13}C^{117/119}Sn)| = 239.51/250.41$ Hz), 110.54 ($Sn(CH_2CH{=}\mathit{C}H_2)_3$, $|^3J(^{13}C^{119}Sn)|$ = not detected), 137.01 ($Sn(CH_2\mathit{C}H{=}CH_2)_3$, $|^2J(^{13}C^{119}Sn)| = 45.78$ Hz). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −34.23. MS MALDI-TOF (2-(4-hydroxiphenylazo)benzoic acid (HABA), THF): 1131 $[M + Na]^+$ (calcd 1131). Anal. Calcd for $C_{44}H_{76}SiSn_4$ (1107.93): C, 47.70; H, 6.91. Found: C, 47.39; H, 6.73.

$Si[(CH_2)_2Sn(CH_2CH_2CH{=}CH_2)_3]_4$ (7). To a solution of $Si[(CH_2)_2SnBr_3]_4$ (4.0 g, 2.55 mmol) in THF (50 mL) was added a solution of $CH_2{=}CHCH_2CH_2MgBr$ in THF (113.7 mL, 0.35 M, 39.78 mmol) at 0 °C. Workup similar to that used for the synthesis of **5** afforded **7** as a yellowish, viscous oil (2.71 g, 83%). IR (KBr, film): $\nu(C{=}C)$ 1639 cm^{-1}(s). ^1H NMR (200.13 MHz, $CDCl_3$): δ 0.67−0.77 (m, 16H, $SiCH_2CH_2Sn$), 0.95 (t, 24H $Sn(C\mathit{H}_2CH_2CH{=}CH_2)_3$, $|^2J(^{13}H^{117/119}Sn)| = 45.78/47.93$ Hz), 2.20−2.37 (m, 24H, $Sn(CH_2C\mathit{H}_2CH{=}CH_2)_3$), 4.86−5.08 (m, 24H, $Sn(CH_2CH_2CH{=}C\mathit{H}_2)_3$), 5.75−5.99 (m, 12H, $Sn(CH_2CH_2C\mathit{H}{=}CH_2)_3$). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ 1.33 ($CH_2\mathit{C}H_2Sn$, $|^1J(^{13}C^{117/119}Sn)| = 305.45/319.62$ Hz), 6.64 ($\mathit{C}H_2CH_2Sn$, $|^2J(^{13}C^{119}Sn)| = 31.\ 61$ Hz), 8.15 ($Sn(\mathit{C}H_2CH_2CH{=}CH_2)_3$, $|^1J(^{13}C^{117/119}Sn)| = 289.65/303.00$ Hz), 30.90 ($Sn(CH_2\mathit{C}H_2CH{=}CH_2)_3$, $|^2J(^{13}C^{119}Sn)| = 17.71$ Hz), 112.97 ($Sn(CH_2CH_2CH{=}\mathit{C}H_2)_3$, $|^4J(^{13}C^{119}Sn)|$ = not detected), 141.93 ($Sn(CH_2CH_2\mathit{C}H{=}CH_2)_3$, $|^3J(^{13}C^{119}Sn)| = 48.77$ Hz). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −3.07. MS MALDI-TOF (IAA, THF): 1384.61 $[M + Ag]^+$ (calcd 1384.19), 1430.43 $[M + 2Na + Ag]^+$ (calcd 1430.19). Anal. Calcd for $C_{56}H_{100}SiSn_4$ (1276.26): C, 52.70; H, 7.90. Found: C, 52.47; H, 7.69.

$Si\{(CH_2)_2Sn[(CH_2)_4GePh_3]_3\}_4$ (8). In analogy with the synthesis of **4**, Ph_3GeH (4.66 g, 15.28 mmol), AIBN (0.13 g, 5 mol %, 0.79 mmol), and **7** (1.30 g, 1.02 mmol) were reacted to afford **8** as a viscous, white oil (3.60 g, 72%). ^1H NMR (400.13 MHz, $CDCl_3$): δ 0.53−0.60 (m, 16H, $SiCH_2CH_2$), 0.60−0.73 (m, 24H, $SnC\mathit{H}_2CH_2CH_2CH_2$), 1.33−1.60 (m, 72H, $SnCH_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2$), 7.22−7.42 (m, 108H, $Ph{-}H^{meta/para}$), 7.43−7.58 (m, 72H, $Ph{-}H^{ortho}$). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 0.47 ($SiCH_2$), 6.44 ($SiCH_2\mathit{C}H_2$), 8.29 ($Sn\mathit{C}H_2CH_2CH_2CH_2$, $|^1J(^{13}C^{117/119}Sn)| = 288.88/302.17$ Hz), 13.65 ($SnCH_2CH_2CH_2\mathit{C}H_2$, $|^4J(^{13}C^{119}Sn)|$ = not detected), 29.85 ($SnCH_2CH_2\mathit{C}H_2CH_2$, $|^3J(^{13}C^{119}Sn)| = 54.84$ Hz), 30.94 ($SnCH_2\mathit{C}H_2CH_2CH_2$, $|^2J(^{13}C^{119}Sn)| = 18.82$ Hz), 128.12 ($Ph{-}C^{meta}$), 128.78 ($Ph{-}C^{para}$), 134.90 ($Ph{-}C^{ortho}$), 137.29 ($Ph{-}C^{ipso}$). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −7.35. MS MALDI-TOF (IAA, THF): 4958.20 $[M + Na]^+$ (calcd 4958.47), 4783.9 $[M - 2C_6H_5]^+$. Anal. Calcd for $C_{272}H_{292}Ge_{12}SiSn_4$ (4935.24): C, 66.20; H, 5.96. Found: C, 65.88; H, 5.71.

$Si\{(CH_2)_2Sn[(CH_2)_4SnPh_3]_3\}_4$ (9). In analogy with the synthesis of **4**, Ph_3SnH (4.95 g, 14.10 mmol), AIBN (0.12 g, 5 mol %, 0.73 mmol), and **7** (1.20 g, 0.94 mmol) were reacted to yield **9** as a viscous, yellowish oil (3.24 g, 63%). ^1H NMR (400.13 MHz, $CDCl_3$): δ 0.53−0.60 (m, 16H, $SiCH_2CH_2$), 0.60−0.73 (m, 24H, $SnC\mathit{H}_2CH_2CH_2CH_2$), 1.33−1.60 (m, 72H, $SnCH_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2$), 7.22−7.42 (m, 108H, $Ph{-}H^{meta/para}$), 7.43−7.58 (m, 72H, $Ph{-}H^{ortho}$). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 0.75 ($SiCH_2$), 6.55 ($SiCH_2\mathit{C}H_2$), 8.16 ($Sn\mathit{C}H_2CH_2CH_2CH_2SnPh_3$, $|^1J(^{13}C^{117/119}Sn)| = 286.92/301.91$ Hz), 10.60 ($SnCH_2CH_2CH_2\mathit{C}H_2SnPh_3$, $|^1J(^{13}C^{117/119}Sn)| = 376.02/393.73$ Hz), 31.47 ($SnCH_2CH_2\mathit{C}H_2CH_2SnPh_3$, $|^2J(^{13}C^{119}Sn)| = 22.07$ Hz, $|^3J(^{13}C^{119}Sn)| = 57.77$ Hz), 31.88 ($SnCH_2\mathit{C}H_2CH_2CH_2SnPh_3$, $|^2J(^{13}C^{119}Sn)| = 18.80$ Hz, $|^3J(^{13}C^{119}Sn)| = 64.03$ Hz), 128.41 ($Ph{-}C^{meta}$, $|^3J(^{13}C^{119}Sn)| = 47.14$ Hz), 128.75 ($Ph{-}C^{para}$, $|^4J(^{13}C^{119}Sn)| = 11.99$ Hz), 139.03 ($Ph{-}C^{ipso}$, $|^1J(^{13}C^{117/119}Sn)| = 458.86/480.11$ Hz), 136.97 ($Ph{-}C^{ortho}$, $|^2J(^{13}C^{119}Sn)| = 34.88$ Hz), $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): δ −7.24 (Sn_{int}), −99.31 (Sn_{periph}). MS MALDI-TOF (IAA, THF): 5510.9 $[M + Na]^+$ (calcd 5511.7), 5621.2 $[M + Na + Ag]^+$ (calcd 5619.5). Anal. Calcd for $C_{272}H_{292}SiSn_{16}$ (5488.44l): C, 59.53; H, 5.36. Found: C, 59.10; H, 5.14.

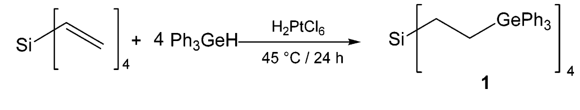
Results and Discussion

The goal of our investigations was to synthesize metallodendrimers of the second generation containing different group 14 elements. For that purpose, we started with the synthesis of first-generation silicon-centered dendrimers having terminal triorganogermanium or triorganotin groups, which in turn could be further functionalized.

Synthesis of Si/Ge Dendrimers. In analogy with the synthesis of tetrakis[2-(triphenylstannyl)ethyl]silane,[17] we obtained the corresponding germanium derivative $Si(CH_2CH_2GePh_3)_4$ (**1**) by hydrogermylation of tetravinylsilane with triphenylgermane. In the presence of H_2PtCl_6 triphenylgermane adds cleanly to the olefinic ligands of the educt following the anti-Markownikow rule, thus affording **1** in almost quantitative yields. The course of the reaction can easily be controlled by IR spectroscopy. The signal of the vinyl double bond of the educt decreases continuously and disappears completely after 24 h. To facilitate the mixing of the reactants by stirring despite the absence of a solvent, the reaction was carried out at 45 °C, that means above the melting point of Ph_3GeH. This hydrogermylation reaction runs slower than the analogous hydrostannylation of tetravinylsilane[17] (Scheme 1).

Compound **1** could be isolated in high purity after workup with pentane as an air- and moisture-stable white solid that melts at 166 °C without decomposition. It is soluble in tetrahydrofuran, toluene, and halogenated hydrocarbons but insoluble in alkanes and diethyl ether. The ^1H NMR spectrum shows two multiplet signals for the ethylene groups at 0.68 to 0.80 ($SiCH_2$) and 1.22

Scheme 1



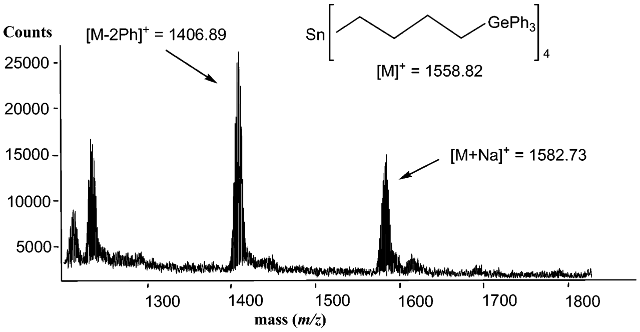
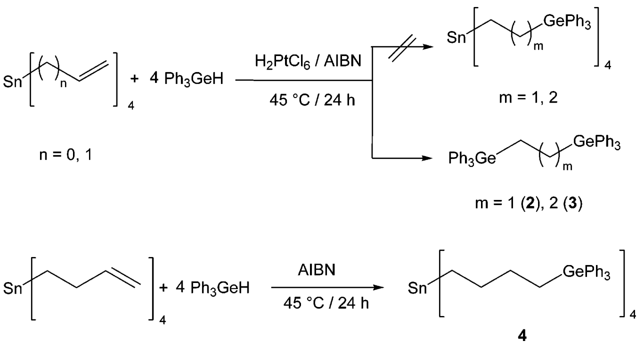


Figure 1. MALDI-TOF mass spectrum of tetrakis[4-(triphenylgermyl)butyl]stannane (**4**).

Scheme 2



to 1.34 ppm ($GeCH_2$), and the $^{13}C\{^1H\}$ NMR spectrum also reflects the constitution of the compound, revealing two sharp resonances at 4.30 and 6.70 ppm for the silicon- and germanium-bonded ethylene groups, respectively. In the MALDI-TOF mass spectrum appear signals at *m/z* 1379.8 (calcd 1379.3) and 1419.8 (calcd 1418.3), corresponding to the molecular ions $[M + Na]^+$ and $[M + Na + K]^+$. No significant fragmentation was observed. The attempts to grow dendrimers of the second generation via functionalization of the outer triphenylgermanium groups of **1** failed. Bromination of **1** did not afford isolable uniform products.

Synthesis of Sn/Ge Dendrimers. Tetravinyl- and tetraallylstannane react with Ph_3GeH in the presence of 5 mol % of azoisobutyronitrile (AIBN) to give the redistribution products $Ph_3GeCH_2CH_2GePh_3$ (**2**) and $Ph_3GeCH_2CH_2CH_2GePh_3$ (**3**)[20] instead of the expected hydrogermylation products tetrakis[2-(triphenylgermyl)ethyl]stannane and tetrakis[2-(triphenylgermyl)propyl]stannane (Scheme 2). Variation of the reaction temperature, use of other solvents, changing the stoichiometry, or using other catalysts did not result in the formation of even traces of the desired dendrimers.[21] The hydrostannylation of tetravinyl- and tetraallylstannane with Ph_3SnH runs in a similar way.[15]

In contrast to the results described above and again in analogy with our earlier investigations on corresponding hydrostannylation reactions,[16] tetra(but-3-enyl)stannane reacts with triphenylgermane in the presence of 5 mol % of AIBN, yielding tetrakis[4-(triphenylgermyl)butyl]stannane (**4**) (Scheme 2). The pure white solid obtained in almost quatitative yields is soluble in all commonly used organic solvents except alkanes and diethyl ether. It is stable in air and water and melts at 121 °C.

The ^1H NMR spectrum of **4** shows two multiplets for the butyl chain at 0.51−0.70 ($SnCH_2$) and 1.31−1.54 ppm ($CH_2CH_2CH_2CH_2GePh_3$).

The magnitudes of the $J(^{13}C^{117/119}Sn)$ coupling constants observed for the methylene group resonances in the $^{13}C\{^1H\}$ NMR spectrum of **4** allow the assignment of the signals according to the generally established series $|^1J| > |^3J| > |^2J| > |^4J|$, but in this connection it is worth noting that the ^{119}Sn coupling signals of the CH_2 group, at a distance of four bonds from the tin atom and bonded to the germanium atom, could not be detected: δ (ppm) 8.43 ($SnCH_2$, $|^1J(^{13}C^{117/119}Sn)| =$ 296.25/310.23 Hz), 29.77 ($SnCH_2CH_2CH_2$, $|^3J(^{13}C^{117/119}Sn)| =$ 54.84 Hz), 30.86 ($SnCH_2CH_2$, $|^2J(^{13}C^{119}Sn)| =$ 19. 36 Hz), and 13.66 ($SnCH_2CH_2CH_2CH_2Ge$, $|^4J(^{13}C^{119}Sn)| =$ not detected).

The $^{119}Sn\{^1H\}$ NMR spectrum shows only one signal at −11.80 ppm, improving the uniformity of the dendrons and their proposed empirical formula.

The MALDI-TOF mass spectrum confirms the constitution of the molecule according to a signal at $m/z = 1582.73$ for $[M + Na]^+$. The absence of signals for molecules being only partially hydrogermylated proves the structural uniformity of the compound. The signal at $m/z = 1406.89$ corresponds to a

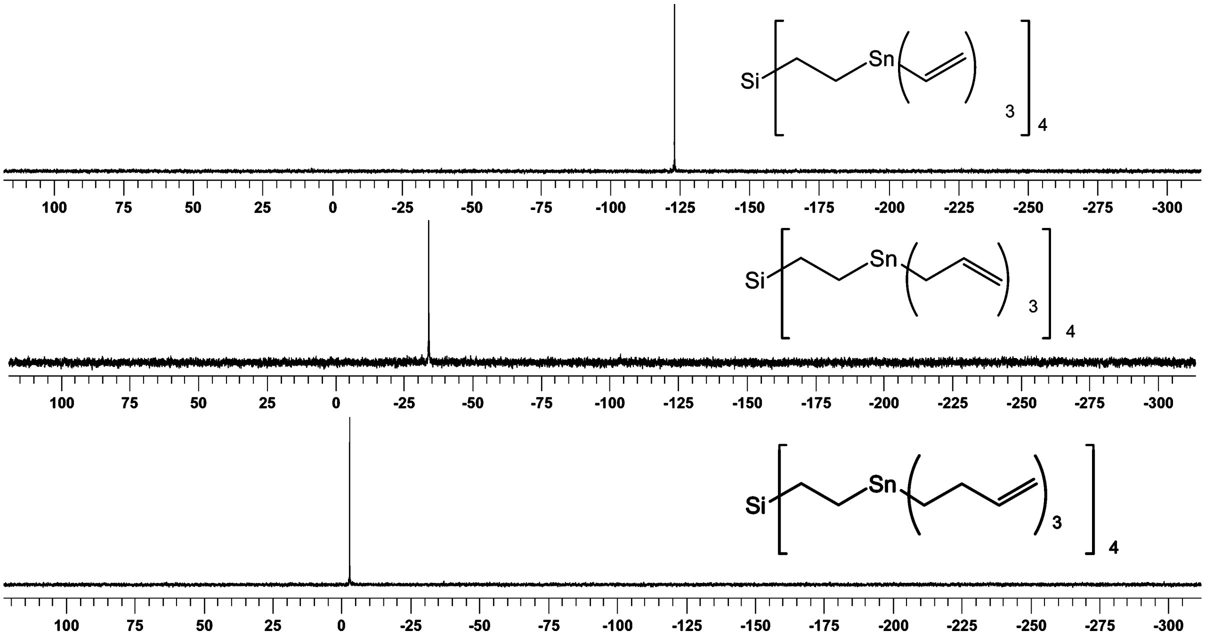


Figure 2. $^{119}Sn\{^1H\}$ NMR spectra of compounds **5**, **6**, and **7** in $CDCl_3$.

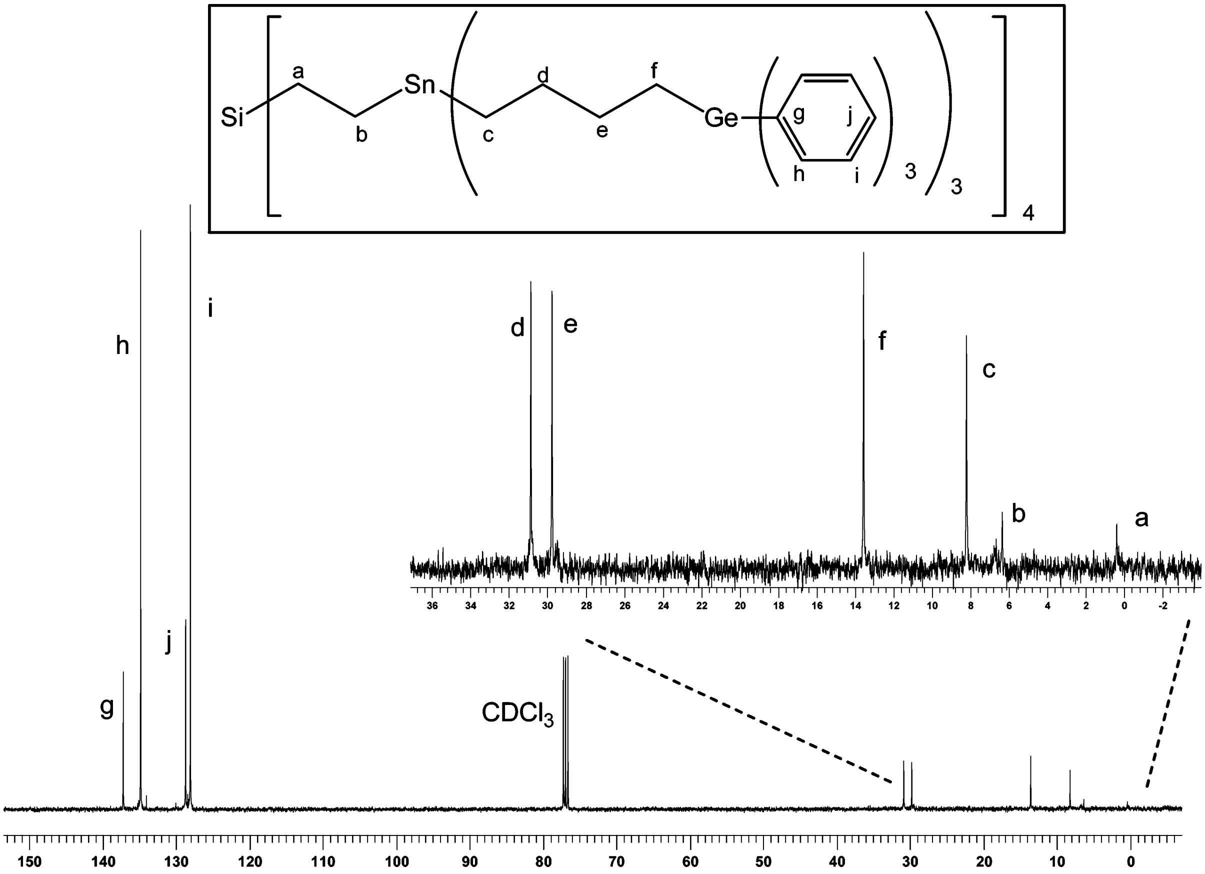
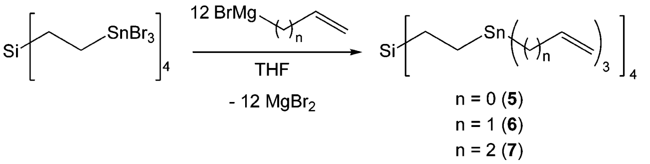
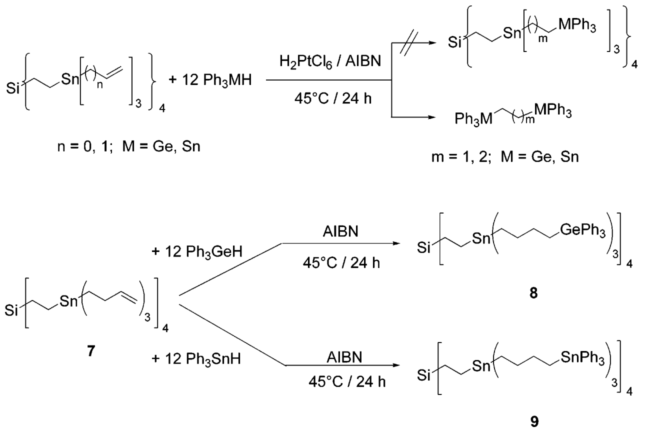


Figure 3. $^{13}C\{^{1}H\}$ NMR spectrum of tetrakis{2-[tris{4-(triphenylgermyl)butyl}stannyl]ethyl}silane (**8**) in $CDCl_3$.

Scheme 3



Scheme 4



fragment formed by the loss of two phenyl groups by Ge−C bond cleavage (Figure 1).

Until now, we did not succeed in preparing dendrimers of the second generation via substitution of the 12 germanium bonded phenyl groups by, for example, bromine.

Synthesis of Si/Sn/Ge Dendrimers. To grow dendrimers of the second generation containing three different group 14 elements, we used the divergent route and started with tetrakis-[2-(tribromostannyl)ethyl]silane,[13a] which was converted to tetrakis[2-(trivinylstannyl)ethyl]silane (**5**), tetrakis[2-(triallylstannyl)ethyl]silane (**6**), and tetrakis[2-(tributenylstannyl)ethyl]silane (**7**) by reaction with the appropriate Grignard reagents in THF (Scheme 3).

5, **6**, and **7** were isolated in yields of 80 to 90% as light yellow, fairly air- and water-stable oils. Their ^{1}H NMR spectra show the characteristic resonances of the protons of the respective vinyl group as two multiplets in the regions between 5.70 and 6.58 (**5**), 4.60 and 6.10 (**6**), and 4.86 and 5.99 Hz (**7**). The $^{13}C\{^{1}H\}$ NMR spectra display distinguishable signals for all carbon atoms. Except for the signals of the appropriate terminal methylene group, all other signals show ^{119}Sn coupling satellites. Position and intensity of the signals as well as the magnitude of the tin coupling constants allow a clear assignment. The $^{119}Sn\{^{1}H\}$ NMR spectra of **5**, **6**, and **7** (Figure 2) display only one resonance signal, thus confirming the uniform structure of the appropriate dendritic molecules.

Whereas the EI mass spectrum of **5** exhibits the molecular ion peak at *m*/*z* 940.07, the EI mass spectra of **6** and **7** show an extensive fragmentation of the molecules according to the fragility of the allyl- and butenyltin units. However, the MALDI-TOF mass spectra of **6** and **7** reveal the corresponding ion peaks at *m*/*z* 1131 $[M + Na]^+$ (calcd 1131) and *m*/*z* 1384.61 $[M + Ag]^+$ (calcd 1384.19), respectively.

The hydrogermylation as well as the hydrostannylation of **5** and **6** with Ph_3GeH and Ph_3SnH, respectively, did not result in the formation of the expected dendrimers $Si\{(CH_2)_2Sn[(CH_2)_nGePh_3]_3\}_4$ and $Si\{(CH_2)_2Sn[(CH_2)_nSnPh_3]_3\}_4$ ($n = 2, 3$), but afforded $Ph_3Ge(CH_2)_nGePh_3$ ($n = 2$ (**2**), 3 (**3**)[20]) and $Ph_3Sn(CH_2)_nSnPh_3$ ($n = 2$,[22] 3[23]), respectively. In contrast, **7** reacts with Ph_3GeH and Ph_3SnH in the desired way, forming tetrakis-

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[21] Aksu, Y. Ph.D. Thesis, Technische Universität Berlin, Berlin, Germany, 2005.

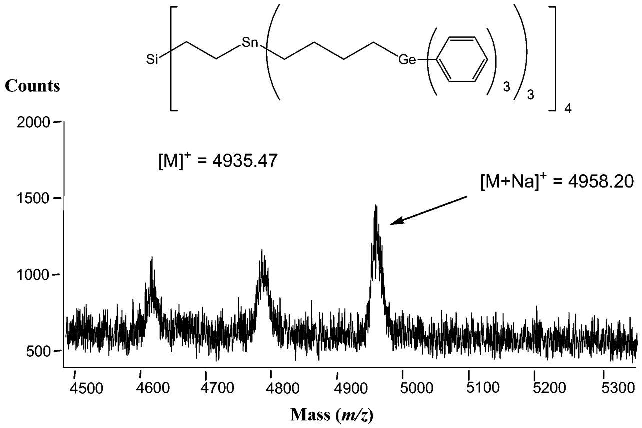

Figure 4. MALDI-TOF mass spectrum of $Si\{(CH_2)_2Sn[(CH_2)_4GePh_3]_3\}_4$ (**8**).

{2-[tris{4-(triphenylgermyl)butyl}stannyl]ethyl}silane (**8**) and tetrakis{2-[tris{4-(triphenylstannyl)butyl}stannyl]ethyl}silane (**9**), respectively, which were isolated as air-stable viscous oils (Scheme 4). In spite of all efforts, we were not successful in crystallizing these products, until now.

The absence of the resonances belonging to the vinyl part of the starting material and the appearance of five multiplets for the protons of the $SiCH_2CH_2$, $SnCH_2$, $SnCH_2(CH_2)_3$, $PhH^{meta+para}$, and Ph^{ortho} groups with an intensity ratio 4:6:18:27:18 in the ^1H NMR spectra of **8** and **9** reflect the complete hydrometalation of **7**. Further proofs for the clear formation of **8** and **9** are their $^{13}C\{^1H\}$ NMR spectra, which are almost identical with those for the organotin dendrimers of the second-generation $Sn\{(CH_2)_3Sn[(CH_2)_4SnPh_3]_3\}_4$ and $Sn\{(CH_2)_4Sn[(CH_2)_4SnPh_3]_3\}_4$.[16] The spectrum of **8** is depicted in Figure 3.

The $^{119}Sn\{^1H\}$ NMR spectra of **8** and **9** show the resonances for the internal tin atom at −7.35 (**8**) and −7.24 ppm (**9**), respectively. They are slightly shifted to higher fields compared to the chemical shift value of the corresponding tin atom in **4** (−11.8 ppm). The ^{119}Sn chemical shift of the peripheral tin atom in **9** (−99.31 ppm) is in accordance to that in $Sn\{(CH_2)_4Sn[(CH_2)_4SnPh_3]_3\}_4$ (−98.88 ppm).[16]

The perfect monodisperse nature of both compounds was confirmed by their MALDI-TOF mass spectra, displaying signals for the molecular ions augmented by sodium at *m*/*z* 4958.20 for **8** and 5510.9 for **9**. In the case of **8**, there are also fragmentation peaks corresponding to the successive loss of two phenyl groups from the germanium atom. Significant peaks attributable to impurities or defect structures were not detected (Figure 4).

Conclusion

Novel first-generation silicon- and tin-centered dendrimers carrying peripheral triphenylgermanium and trivinyl-, triallyl-, and tributenyltin groups have been prepared by hydrogermylation of $Si(CH{=}CH_2)_4$ and $Sn(CH_2CH_2CH{=}CH_2)_4$ and by metathetical reactions of $Si(CH_2CH_2SnBr_3)_4$ with the Grignard reagents RMgBr ($R = CH{=}CH_2$, $CH_2CH{=}CH_2$, $CH_2CH_2CH{=}CH_2$). ^1H, ^{13}C, and ^{119}Sn NMR spectroscopic as well as MALDI-TOF mass spectrometric investigations evidenced that all synthetic steps proceed efficiently without steric hindrance and competitive reactions. It could be demonstrated that only the first-generation dendrimer with peripheral tributenyltin groups could be hydrometalated to give $Si\{(CH_2)_2Sn[(CH_2)_4GePh_3]_3\}_4$ and $Si\{(CH_2)_2Sn[(CH_2)_4SnPh_3]_3\}_4$ as the first metallodendrimers of the second generation containing different group 14 elements.

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