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Synthesis and characterization of α, ω-bis [tri - (w - triphenylstannyl) butylstannyl] alkanes as starting materials for organotin dendrimers

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$Ph_3Sn(CH_2)_mCH{=}CH_2$ [m = 2 (1a), 3 (1b)] reacts with Ph_3SnH, yielding $Ph_3Sn(CH_2)_nSnPh_3$ [n = 4 (2a), 5 (2b)], which in turn reacts with CH_3COOH or HCl, producing $(CH_3CO_2)_3Sn(CH_2)_nSn(O_2CCH_3)_3$ (3a, b) and $Cl_3Sn(CH_2)_nSnCl_3$ (4a, b), respectively. Alkylation of compounds 4 with $BrMg(CH_2)_2CH{=}CH_2$ affords $(CH_2{=}CHCH_2CH_2)_3Sn(CH_2)_nSn(CH_2CH_2CH{=}CH_2)_3$ (5a,b). Hydrostannylation of 5a, b with Ph_3SnH results in the formation of $[Ph_3Sn(CH_2)_4]_3Sn(CH_2)_nSn[(CH_2)_4SnPh_3]_3$ (6a, b) which on agitation with HCl gives $[ClPh_2Sn(CH_2)_4]_3Sn(CH_2)_nSn[(CH_2)_4SnPh_2Cl]_3$ (7a, b). Hydrogenation of 7a and 7b with $LiAlH_4$ leads to $[HPh_2Sn(CH_2)_4]_3Sn(CH_2)_nSn[(CH_2)_4SnPh_2H]_3$ (8a, b), which on further reaction with $CH_2{=}CHCH_2OH$ yields $[HO(CH_2)_3Ph_2Sn(CH_2)_4]_3Sn(CH_2)_nSn[(CH_2)_4SnPh_2(CH_2)_3OH]_3$ (9a, b). All compounds were characterized by multinuclear NMR studies (^1H, ^{13}C, ^{119}Sn), mass spectrometry (MALDI-TOF, EI) and elemental analyses.

KEYWORDS: dendrimers; organotin compounds; NMR; MS

INTRODUCTION

Metallodendrimers are of current interest because of their high potential as precursors for new materials.[1–5] In contrast to the preparation of pure organic dendrimers, the synthesis of metallodendrimers, especially of those containing covalent metal–carbon bonds, 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,[6–12] only a few reports concerning the synthesis of main group metal based dendrimers have been published so far.[13–23] Recently, we opened up the field of organotin dendrimers[24–29] especially in view of their use as iodine-free X-ray contrast agents.[30] For that purpose, the content of tin of the target molecules should be as high as possible. Until now, we did not succeed in the preparation of first-generation tin-centered dendrimers $Sn[(CH_2)_nSnR_3]_4$ with $n \leq 3$. In addition, all our efforts to achieve complete substitution of the phenyl groups bonded to the peripheral tin atoms in the second-generation tin-centered dendrimers $Sn\{(CH_2)_nSn[(CH_2)_4SnPh_3]_3\}_4$ (n = 3, 4) resulted in the formation of mixtures of different incompletely substituted and inseparable compounds.[27] Third-generation tin-centered dendrimers are not available by this route.

Another possibility to get dendrimers containing a high percentage of tin is to start with alkyl-bridged ditin hexaalkenides $(C_nH_{2n-1})_3Sn(CH_2)_mSn(C_nH_{2n-1})_3$ as a core. Distannylated alkyl compounds including compounds with short alkyl spacers have been known since 1930[31] and compounds containing aromatic spacers have been known since as early as 1925.[32] Recently, Dakternieks and co-workers[33] and Jousseaume *et al*.[34] investigated α,ω-ditin hexaalkenides and arylides as starting compounds for new materials. Here we describe the synthesis and characterization of two new α, ω-bis [tri - (w - triphenylstannyl) butylstannyl] alkanes and some of their derivatives as starting materials for organotin dendrimers.

RESULTS AND DISCUSSION

The goal of our investigations was to synthesize cores for organotin dendrimers containing two tin atoms with

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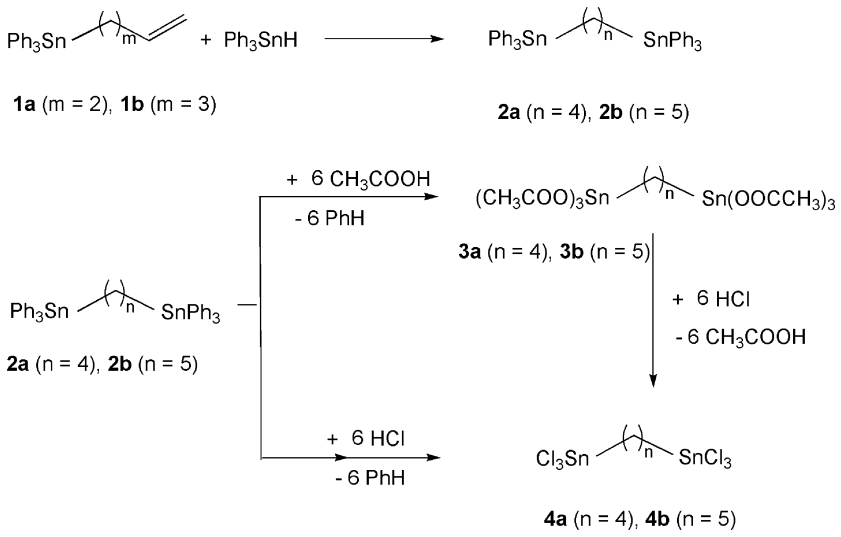
substituents accessible for further reactions to build up second-generation dendrimers with a high tin content. In consideration of our earlier results,[26,27,29] demonstrating that hydrostannylation of vinyl and allyl tin compounds is accompanied by unwanted redistribution reactions, we chose 1,4-bis(tribut-3-enylstannyl)butane and 1,5-bis(tribut-3-enylstannyl)pentane as starting materials.

1,4-Bis(tribut-3-enylstannyl)butane and 1,5-bis(tribut-3-enylstannyl)pentane

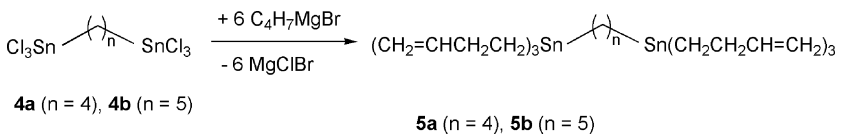
3-Butenyl(triphenyl)stannane (**1a**)[35,36] and 4-pentenyl (triphenyl)stannane (**1b**)[35,37] react with triphenylstannane in toluene in the presence of AIBN with formation of 1,4-bis(triphenylstannyl)butane (**2a**)[38–42] and 1,5-bis(triphenylstannyl)pentane (**2b**),[38,41,43,44] as white and light brown solids, respectively. The further reactions of **2a** and **2b** with anhydrous glacial acetic acid at 110 °C or with anhydrous HCl in diethyl ether at −78 °C run with substitution of all six tin-bonded phenyl groups by acetyl or chloride ligands, yielding 1,4-bis(triacetoxistannyl)butane (**3a**) and 1,5-bis(triacetoxistannyl)pentane (**3b**) or 1,4-bis(trichlorostannyl)butane (**4a**)[33,34] and 1,5-bis(trichlorostannyl)pentane (**4b**)[33,34] as light brown solid and viscous brownish oil, respectively. The bis(trichlorostannyl)alkanes **4a** and **4b** are also available by the reactions of **3a** and **3b** with HCl (Scheme 1).

Compounds **1a, b, 2a, b** and **4a, b** have already been described in the literature, but have not been completely characterized. Therefore the missing NMR and MS data of these compounds are given in the Experimental. The respective values of the ^{1}H and ^{13}C NMR chemical shifts and coupling constants are in the expected range and need no further discussion. The new compounds **3a, b** could be isolated in yields of 90% as white (**3a**) and yellowish solids (**3b**), which are stable against air and moisture. They are soluble in tetrahydrofuran, toluene and halogenated hydrocarbons. Their ^{1}H NMR spectra show a singlet for the CH_3 protons of the six acetyl groups at 2.12 (**3a**) and 2.08 ppm (**3b**), a multiplet in the ranges 1.35–1.57 (**3a**) and 1.20–1.50 ppm (**3b**) for the tin-bonded methylene groups and a further multiplet between 1.59 and 1.86 (**3a**) and 1.53 and 1.81 ppm (**3b**) for the remaining two (**3a**) and three (**3b**) bridging CH_2 groups. The $^{13}C\{^{1}H\}$NMR spectra also reflect the constitution of the compounds. Besides the signals of the bridging carbon atoms, they reveal sharp resonances at 18.35 and 184.44 (**3a**) and at 20.19 and 181.44 ppm (**3b**) for the respective methyl and carboxyl carbon atoms of the acetoxy ligand. The $^{119}Sn\{^{1}H\}$NMR spectra show only one signal at −540.07 (**3a**) and −555.75 ppm (**3b**).

1,4-bis(trichlorostannyl)butane (**4a**) and 1,5-bis(trichlorostannyl)pentane (**4b**) react with six equivalents of but-3-enylmagnesium bromide in THF at 0 °C to give the corresponding hexaalkenylated derivatives 1,4-bis(tribut-3-enylstannyl)butane (**5a**) and 1,5-bis(tribut-3-enylstannyl)



Scheme 1. Synthesis of compounds **4a, b**.



Scheme 2. Synthesis of compounds **5a, b**.

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pentane (**5b**) in yields of 88 and 93%, respectively, as yellow oils which could not be crystallized (Scheme 2).

The ^{1}H NMR spectra of **5a** and **5b** show broad multiplets for the CH_2 protons of the butylene and pentylene chain bridging the two tin atoms and for the CH_2═$CHCH_2$ protons of the butenyl groups. In the spectra of both compounds, the α-CH_2 groups of the alkenyl ligands give rise for a triplet at 0.93 ppm [$^2J(^1H^{117/119}Sn) = 23.21/24.29$ Hz]. The magnitudes of the $J(^{13}C^{117/119}Sn)$ coupling constants observed for the methylene group resonances in the $^{13}C\{^1H\}$NMR spectra of **5a** and **5b** allow the assignment of the signals according to the generally established series $|^1J| > |^3J| > |^2J| > |^4J|$. However, it should be noted that the ^{119}Sn coupling signals of the CH_2 group, being in a distance of four bonds from the tin atom, could not be detected. The $^{119}Sn\{^1H\}$NMR spectra show only one signal at −6.97 (**5a**) and −7.21 ppm (**5b**), confirming the purity of both compounds.

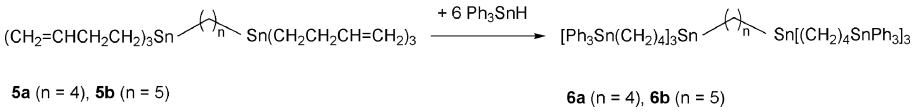
1,4-Bis[tri-(4-triphenylstannyl)butylstannyl] butane and 1,5-bis[tri-(4-triphenylstannyl) butylstannyl]pentane

To grow dendrimers of the first generation containing two tin metals in the core, we used the divergent route and started with 1,4-bis(tribut-3-enylstannyl)butane (**5a**) and 1,5-bis(tribut-3-enylstannyl)pentane (**5b**), which were hydrostannylated by Ph_3SnH to give 1,4-bis[tri-(4-triphenylstannyl)butylstannyl]butane (**6a**) and 1,5-bis[tri-(4-triphenylstannyl)butylstannyl]pentane (**6b**) (Scheme 3). The compounds were isolated in yields of 76% (**6a**) and 60% (**6b**) as white, viscous, fairly air- and water-stable oils.

Their ^{1}H NMR spectra show multiplets for the protons of the 18 phenyl groups and for the protons of the four respective five-membered CH_2-chains between the two tin atoms. The $^{13}C\{^1H\}$NMR spectra display distinguishable signals for all carbon atoms. Except the signals of the carbon atoms forming the bridge between the two tin atoms, all other signals show $^{117/119}$Sn coupling satellites. The position and the intensity of the signals as well as the magnitude of the tin coupling constants allow a clear assignment. Each of the $^{119}Sn\{^1H\}$NMR spectra displays two signals, one at −11.35 ppm (**6a**) and −11.58 ppm (**6b**) for the two tin atoms in the core and the other at −99.50 ppm (**6a**) and −99.07 ppm (**6b**) for the six tin atoms in the periphery (Fig. 1).

The MALDI-TOF mass spectra of **6a** and **6b** reveal the corresponding ion peaks at m/z 2753.33 $[M + Na]^+$ (calcd 2753.3) and 2862.6 $[M + Na + Ag]^+$ (calcd 2861.2) for **6a** and 2767.35 $[M + Na]^+$ (calcd 2767.4) and 2875.3 $[M + Na + Ag]^+$ (calcd 2875.2) for **6b**, respectively (Fig. 2).

Our intensive attempts to replace all 18 phenyl groups from the peripheral tin atoms of **6a** and **6b** by reaction with ethereal HCl did not result in the formation of the desired, completely substituted compounds until now. However, **6a** and **6b** react with exactly the 6-fold amount of HCl, forming the monosubstitued derivatives $[ClPh_2Sn(CH_2)_4]_3Sn(CH_2)_nSn[(CH_2)_4SnPh_2Cl]_3$ (**7a** and **7b**) as light yellow viscous oils. Compounds **7a** and **7b** react with $LiAlH_4$ in diethyl ether, forming the corresponding hydrides $[Ph_2(H)Sn(CH_2)_4]_3Sn(CH_2)_nSn[(CH_2)_4Sn(H)Ph_2]_3$ (**8a** and **8b**) as colorless viscous oils. All six Sn−H functions of **8a** and **8b**, respectively, hydrostannylate allylic alcohol yielding $\{[HO(CH_2)_3]Ph_2Sn(CH_2)_4\}_3Sn(CH_2)_nSn\{(CH_2)_4SnPh_2[(CH_2)_3OH]\}_3$ (**9a** and **9b**) (Scheme 4).



Scheme 3. Synthesis of compounds **6a, b**.

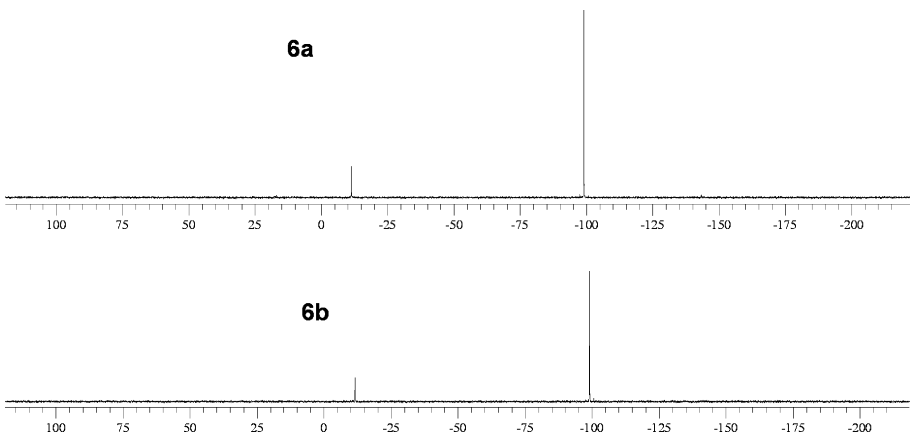


Figure 1. $^{119}Sn\{^1H\}$NMR spectra of compounds **6a** and **6b** in $CDCl_3$.

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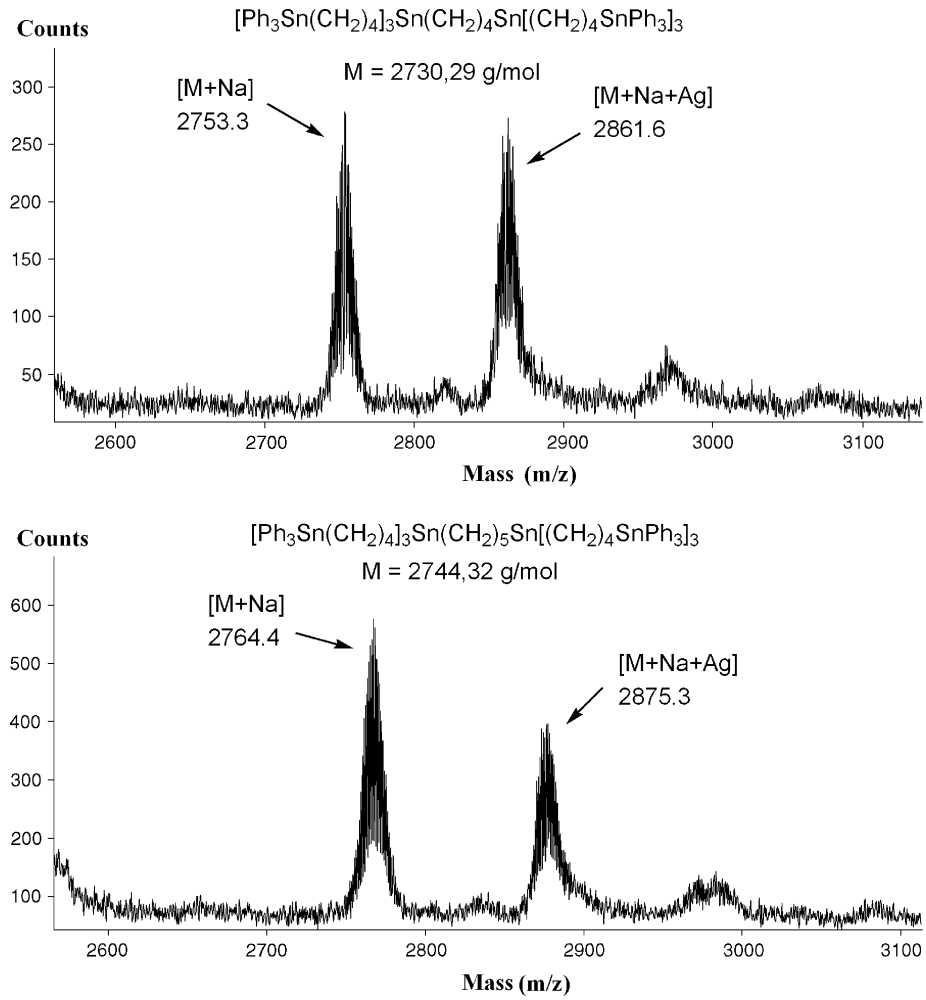
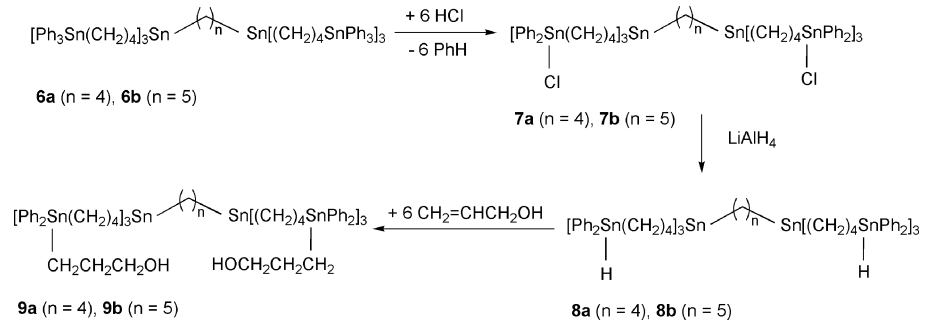


Figure 2. MALDI-TOF mass spectra of **6a** and **6b**.



Scheme 4. Synthesis of compounds **7a, b, 8a, b** and **9a, b**.

These first-generation dendrimers **6a, b, 7a, b, 8a, b**, and **9a, b** could not be crystallized, thus excluding X-ray structural determination. However, the purity and the correctness of the proposed structures of the compounds were proved by their NMR and MALDI-TOF spectra. They are potential starting materials for the synthesis of dendrimers of the second generation. Further work in this area is in progress.

EXPERIMENTAL

General

All manipulations involving air-sensitive compounds were carried out in dry, oxygen-free solvents under an inert atmosphere of nitrogen using standard Schlenk techniques. Melting points were measured in sealed capillaries with

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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 (^{1}H, 200 MHz; ^{13}C, 50.32 MHz) and ARX 400 (^{1}H, 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 ^{1}H and ^{13}C residues of the deuterated solvents (^{1}H and ^{13}C) and to $Sn(CH_3)_4$ (^{119}Sn), respectively. IR spectra were obtained 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 M 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 of CH_3COONa, KCl or AgI were used as ionization agents. Sonification was applied to speed up mixing. One µl 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.

Ph_3SnCl, AIBN, $BrCH_2CH_2CH{=}CH_2$, $BrCH_2CH_2CH_2CH{=}CH_2$, $LiAlH_4$, Mg and anhydrous HCl(g) were used as purchased, Ph_3SnH[45] was prepared according to published procedures.

But-3-enyl(triphenyl)stannane, ***1a***

A solution of Ph_3SnCl (10.6 g, 27.50 mmol) in THF (50 ml) was treated with 36.70 ml (27.50 mmol) of a 0.75 M solution of $BrMgCH_2CH_2CH{=}CH_2$ in THF at 0 °C. After stirring for 5 h at room temperature the reaction mixture was cooled to 0 °C and then hydrolyzed cautiously with water. The aqueous fraction was extracted with diethyl ether. The combined organic phases were washed several times with a saturated aqueous NH_4Cl solution and dried over Na_2SO_4. After removal of all volatiles **1a** was obtained as light yellow solid. Yield: 9.25 g (83%).

$^{13}C\{^1H\}$ NMR (50.32 MHz; $CDCl_3$): $\delta = 9.99$ [$|^1J(^{13}C^{117/119}Sn)| = 187.1/195.7$ Hz, $SnCH_2$], 30.38 [$|^2J(^{13}C^{119}Sn)| = 9.7$ Hz, $SnCH_2CH_2$], 113.84 ($C{=}CH_2$), 128.48 [$|^3J(^{13}C^{119}Sn)| = 24.2$ Hz, Ph-C^{meta}], 128.87 [$|^4J(^{13}C^{119}Sn)| = 5.5$ Hz, Ph-C^{para}], 137.08 [$|^2J(^{13}C^{119}Sn)| = 17.7$ Hz, Ph-C^{ortho}], 138.82 [$|^1J(^{13}C^{117/119}Sn)| = 233.3/244.1$ Hz, Ph-C^{ipso}], 141.15 [$|^3J(^{13}C^{119}Sn)| = 31.2$ Hz, $CH{=}CH_2$]; $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): $\delta = -98.98$.

Pent-3-enyl(triphenyl)stannane, ***1b***

In analogy to the synthesis of **1a**, a solution of Ph_3SnCl (12.5 g, 32.43 mmol) in THF (50 ml) was treated with 43.2 ml (32.43 mmol) of a 0.75 M solution of $BrMgCH_2CH_2CH_2CH{=}CH_2$ in THF at 0 °C. Appropriate workup gave **1b** as light yellow solid. Yield: 10.60 g (78%).

$^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): $\delta = 10.47$ [$|^1J(^{13}C^{117/119}Sn)| = 188.6/197.3$ Hz, $SnCH_2$], 26.02 [$|^2J(^{13}C^{119}Sn)| = 10.4$ Hz, $SnCH_2CH_2$], 38.15 [$|^3J(^{13}C^{119}Sn)| = 31.6$ Hz, $Sn(CH_2)_2CH_2$], 114.98 ($CH{=}CH_2$), 128.44 [$|^3J(^{13}C^{119}Sn)| = 24.3$ Hz, Ph-C^{meta}], 128.81 [$|^4J(^{13}C^{119}Sn)| = 5.5$ Hz, Ph-C^{para}], 137.01 [$|^2J(^{13}C^{119}Sn)| = 17.7$ Hz, Ph-C^{ortho}], 138.16 ($CH{=}CH_2$), 138.89 [$|^1J(^{13}C^{117/119}Sn)| = 231.3/242.0$ Hz, Ph-C^{ipso}]; $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): $\delta = -99.61$.

1,4-Bis(triphenylstannyl)butane, ***2a***

A solution of **1a** (8.69 g, 21.40 mmol) in toluene (10 ml) was dropped slowly to a stirred solution of Ph_3SnH (8.24 g, 21.40 mmol) and AIBN (0.18 g, 1.07 mmol) in toluene (10 ml). After stirring the reaction mixture for 24 h at ambient temperature pentane (25 ml) was added. The white solid formed was separated, redissolved in toluene (10 ml) and again precipitated by addition of pentane (25 ml). The separated precipitate was washed several times with a mixture of pentane–diethyl ether (1 : 1), then all volatiles were carefully removed in vacuum leaving behind **2a** as white solid. Yield: 11.81 g (73%).

$^{119}Sn\{^1H\}$NMR (149.21 MHz, $CDCl_3$) : $\delta = -99.86$.

1,5-Bis(triphenylstannyl)pentane, ***2b***

Compound **2b** was prepared by a procedure analogous to that for **2a** using 9.30 g (22.19 mmol) of **1b,** 8.55 g (22.19 mmol) of Ph_3SnH and 0.18 g (1.11 mmol) of AIBN. Appropriate workup gave **2b** as light brown solid. Yield: 13.71 g (79%).

^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.49–1.65$ (m, 4H, $SnCH_2$), 1.74–1.90 [m, 6H, $SnCH_2(CH_2)_3$], 7.42–7.51 (m, 18H, Ph-$H^{para/meta}$), 7.60–7.69 (m, 12H, Ph-H^{ortho}); $^{13}C\{^1H\}$ NMR (100.64 MHz, $CDCl_3$): $\delta = 10.81$ [$|^1J(^{13}C^{117/119}Sn)| = 189.1/197.8$ Hz, $SnCH_2$], 25.88 [$|^2J(^{13}C^{119}Sn)| = 10.9$ Hz, $SnCH_2CH_2$], 38.69 [$|^3J(^{13}C^{117/119}Sn)| = 30.0/31.1$ Hz, $Sn(CH_2)_2CH_2$], 128.41 [$|^3J(^{13}C^{117/119}Sn)| = 23.2/24.0$ Hz, Ph-C^{meta}], 128.76 [$|^4J(^{13}C^{119}Sn)| = 5.7$ Hz, Ph-C^{para}], 137.00 [$|^2J(^{13}C^{119}Sn)| = 17.7$ Hz, Ph-C^{ortho}], 139.03 [$|^1J(^{13}C^{117/119}Sn)| = 230.0/240.6$ Hz, Ph-C^{ipso}]; $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): $\delta = -99.64$; MS [100 °C, m/z (%)]: 693 (0.7) [$M - C_6H_5$]$^+$, 623 (0.6) [$M - C_5H_{10} - C_6H_5$]$^+$, 616 (0.4) [$M - 2C_6H_5$]$^+$, 351 (100) [$M - C_5H_{10} - 3C_6H_5 - Sn$]$^+$, 120 (40) [Sn]$^+$.

1,4-Bis(triacetoxistannyl)butane, ***3a***

To 7.5 g (9.92 mmol) of **2a**, anhydrous glacial acetic acid (25 ml) was added drop-wise slowly. The resulting clear reaction mixture was stirred for 24 h at 110 °C. Evaporation of all volatiles in vacuum (10^{-2} mbar) gave **3a** as a white solid. Yield: 5.78 g (90%).

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IR (KBr, film): ν (CO) 1594 cm^{-1} (s); ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.35–1.57$ (m, 4H, $SnCH_2$), 1.59–1.86 [m, 4H, ($SnCH_2CH_2$)], 2.12 [s, 18H, (CH_3CO)]; $^{13}C\{^1H\}$ NMR (100.64 MHz, $CDCl_3$): $\delta = 18.35$ (CH_3C), 26.74 [$|^2J(^{13}C^{117/119}Sn)| = 92.4/96.7$ Hz, $SnCH_2CH_2$], 27.93 [$|^1J(^{13}C^{117/119}Sn)| = 485.8/508.5$ Hz, $SnCH_2$], 184.44 (CH_3CO); $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): $\delta = -540.07$; MS [100 °C, m/z (%)]: 589 (0.3) $[M - CH_3COO]^+$, 487 (0.7) $[M - 2CH_3COO - CO_2]^+$, 297 (4.8) $[M - (CH_3COO)_3Sn - C_4H_8]^+$, 179 (5.6) $[M - (CH_3COO)_3Sn - C_4H_8 - 2CH_3COO]^+$, 120 (0.5) $[Sn]^+$. Anal. calcd for $C_{16}H_{26}O_{12}Sn_2$ (647.79 g/mol): C, 29.67; H, 4.05%. Found: C, 30.07; H, 4.18%.

*1,5-Bis(triacetoxistannyl)pentane, **3b***

In analogy to the synthesis of **3a**, a mixture of **2b** (8.3 g, 10.78 mmol) and anhydrous glacial acetic acid (25 ml) was heated to 110 °C for 24 h. After evaporation of all volatiles, **3b** was isolated as yellowish solid. Yield: 6.35 g (89%).

IR (KBr, film): ν (CO) 1569 cm^{-1} (s); ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.20–1.50$ [m, 4H, ($SnCH_2$)], 1.53–1.81 [m, 6H, ($SnCH_2(CH_2)_2$], 2.08 [s, 18H, (CH_3CO)]; $^{13}C\{^1H\}$ NMR (100.64 MHz, $CDCl_3$): $\delta = 20.19$ (CH_3CO), 23.44 ($SnCH_2CH_2$), 29.61 ($SnCH_2$), 34.77 [$Sn(CH_2)_2CH_2$], 181.44 (CH_3CO); $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): $\delta = -555.75$; MS [100 °C, m/z (%)]: 602 (0.4) $[M - CH_3COO]^+$, 500 (0.2) $[M - 2CH_3COO - CO_2]^+$, 308 (8.4) $[M - (CH_3COO)_3Sn - C_4H_8]^+$, 190 (9.1) $[M - (CH_3COO)_3Sn - C_4H_8 - 2CH_3COO]^+$, 120 (0.6) $[Sn]^+$. Anal. calcd for $C_{17}H_{28}O_{12}Sn_2$ (661.78 g/mol): C, 30.85; H, 4.26%. Found: C, 30.17; H, 4.13%.

*1,4-Bis(trichlorostannyl)butane, **4a***

Method A: to a vigorously stirred solution of **2a** (7.6 g, 10.05 mmol) in CH_2Cl_2 (30 ml) 15.08 ml (60.31 mmol) of a 4 M solution of anhydrous HCl(g) in diethyl ether was added drop-wise at −78 °C within 0.5 h. After stirring the mixture at −78 °C for 5 h, it was allowed to warm up gradually to room temperature and stirring was continued for further 12 h. Then the solvents used and the benzene formed were removed in vacuum (10^{-2} mbar), affording **4a** as light brown solid. Yield: 4.63g (91%).

Method B: in analogy to the procedure described above for method A, **3a** (5.2 g, 8.03 mmol) solved in CH_2Cl_2 (25 ml) reacted with 12.04 ml (48.16 mmol) of a 4 M solution of anhydrous HCl(g) in diethyl ether yielding **4a** as light brownish solid (3.86g, 95%).

^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.99–2.16$ (m, 4H, $SnCH_2CH_2$), 2.30–2.44 [m, 4H, $|^2J(^1H^{117/119}Sn)| = 42.6/44.5$ Hz, $SnCH_2$]; $^{13}C\{^1H\}$ NMR (100.64 MHz, $CDCl_3$): $\delta = 21.18$ [$|^2J(^{13}C^{119}Sn)| = 27.3$ Hz, $SnCH_2CH_2$], 30.39 [$|^1J(^{13}C^{117/119}Sn)| = 325.1/340.3$ Hz, $SnCH_2$]; $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): $\delta = 4.04$; MS [100 °C, m/z (%)]: 470.8 (0.9) $[M - Cl]^+$, 435.6 (0.6) $[M - 2Cl]^+$, 398.8 (0.2) $[M - 3Cl]^+$, 222.8 (27.3) $[M - 3Cl - Sn - C_4H_8]^+$, 120 (7.7) $[Sn]^+$.

*1,5-Bis(trichlorostannyl)pentane, **4b***

Method A: in analogy to the synthesis of **4a**, a solution of 7.21 g (9.22 mmol) of **2b** in CH_2Cl_2 (30 ml) was reacted with 13.83 ml (55.31 mmol) of a 4 M solution of anhydrous HCl(g) in diethyl ether, affording **4b** as brownish viscous oil. Yield: 4.27g (89%).

Method B: in analogy to the synthesis of **4a**, a solution of 6.10 g (9.22 mmol) of **3b** in CH_2Cl_2 (25 ml) was reacted at −78 °C with 13.83 ml (55.30 mmol) of a 4 M solution of anhydrous HCl(g) in diethyl ether, giving **4b** as brownish viscous oil. Yield: 4.46g (93%).

^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.60–1.83$ [m, 2H, $Sn(CH_2)_2CH_2$], 1.98–2.17 (m, 4H, $SnCH_2CH_2CH_2$), 2.36–2.54 [m, 4H, $|^2J(^1H^{117/119}Sn)| = 41.5/43.2$ Hz, $SnCH_2$]; $^{13}C\{^1H\}$ NMR (100.64 MHz, $CDCl_3$): $\delta = 24.18$ [$|^2J(^{13}C^{119}Sn)| = 27.5$ Hz, $SnCH_2CH_2$], 34.67 [$|^1J(^{13}C^{117/119}Sn)| = 318.5/333.0$ Hz, $SnCH_2$], 34.76 [$|^3J(^{13}C^{117/119}Sn)| = 58.0/60.8$ Hz, $Sn(CH_2)_2CH_2$]; $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): $\delta = 6.08$; MS [100 °C, m/z (%)]: 484.8 (9) $[M - Cl]^+$, 449.6 (1.1) $[M - 2Cl]^+$, 414.7 (0.1) $[M - 3Cl]^+$, 379.8 (0.4) $[M - 4Cl]^+$, 342.7 (1.5) $[M - 5Cl]^+$, 307.0 (0.4) $[M - 6Cl]^+$, 120 (2.3) $[Sn]^+$.

*1,4-Bis(tribut-3-enylstannyl)butane, **5a***

To a solution of **4a** (6.0 g, 11.85 mmol) in THF (100 ml) 79 ml (71.11 mmol) of a 0.9 M freshly prepared but-3-enylmagnesium bromide solution in THF was added cautiously at 0 °C within 1 h. The mixture was stirred for 0.5 h at 0 °C and subsequently for 12 h at ambient temperature. After cooling the mixture to 0 °C, it was hydrolyzed slowly with a saturated aqueous NH_4Cl solution. The aqueous fraction was extracted with diethyl ether. The combined organic fractions were washed several times with a saturated aqueous NH_4Cl solution and then dried over Na_2SO_4. After removal of all volatiles **5a** was obtained as light yellow oil. Yield: 6.51 g (88%).

IR (KBr, film): ν (C=C) 1639 cm^{-1} (s); ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 0.93$ [t, 12H, $|^2J(^1H^{117/119}Sn)| = 23.2/24.3$ Hz, $SnCH_2C_3H_5$], 1.43–1.55 [m, 8H, $Sn(CH_2)_4Sn$], 2.19–2.35 (m, 12H, $SnCH_2CH_2C_2H_3$), 4.87–5.07 (m, 12H, $CH{=}CH_2$), 5.76–5.99 (m, 6H, $CH{=}CH_2$); $^{13}C\{^1H\}$ NMR (100.64 MHz, $CDCl_3$): $\delta = 8.32$ [$|^1J(^{13}C^{117/119}Sn)| = 148.5/155.3$ Hz, $SnCH_2C_3H_5$], 9.08 [$|^1J(^{13}C^{117/119}Sn)| = 152.9/160.2$ Hz, $CH_2SnC_4H_7$], 30.86 [$|^2J(^{13}C^{119}Sn)| = 8.7$ Hz, $SnCH_2CH_2C_2H_3$], 31.8 [$|^2J(^{13}C^{119}Sn)| = 10.1$ Hz, $|^3J(^{13}C^{117/119}Sn)| = 26.7/27.8$ Hz, $CH_2CH_2SnC_4H_7$], 112.94 ($CH{=}CH_2$), 141.90 [$|^3J(^{13}C^{117/119}Sn)| = 24.0/25.1$ Hz, $CH{=}CH_2$]; $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): $\delta = -6.97$; MS [100 °C, m/z (%)]: 569.3 (0.2) $[M - C_4H_7]^+$, 514.2 (0.2) $[M - 2C_4H_7]^+$, 459.1 (0.3) $[M - 3C_4H_7]^+$, 404.3 (0.4) $[M - 4C_4H_7]^+$, 349.2(4.8) $[M - 5C_4H_7]^+$, 285.2 (100) $[M - C_4H_8 - Sn - 3C_4H_7]^+$, 229.1 (23) $[M - C_4H_8 - Sn - 4C_4H_7]^+$, 172.7 (27) $[M - C_4H_8 - Sn - 5C_4H_7]^+$, 120.1 (4.3) $[Sn]^+$. Anal. calcd for $C_{28}H_{50}Sn_2$ (624.09 g/mol): C, 53.89; H, 8.08%. Found: C, 53.76; H, 8.05%.

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*1,5-Bis(tribut-3-enylstannyl)pentane, **5b***

In analogy to the synthesis of **5a**, a solution of 5.52 g (10.61 mmol) of **4b** in THF (100 ml) was reacted at 0 °C with 70.73 ml (63.66 mmol) of a 0.9 M solution of but-3-enylmagnesium bromide in THF. After analogous workup, **5b** was isolated as yellowish viscous oil. Yield: 6.30g (93%).

IR (KBr, film): ν (C=C) 1639 cm^{-1} (s); ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 0.93$ [t, 12H, $|^2J(^1H^{117/119}Sn)| = 23.2/24.3$, $SnCH_2C_3H_5$], 1.24–1.39 (m, 4H, $CH_2SnC_4H_7$), 1.42–1.60 {m, 6H, $Sn[CH_2(CH_2)_3CH_2SnC_4H_7]$}, 2.19–2.35 (m, 12H, $SnCH_2CH_2C_2H_3$), 4.87–5.07 (m, 12H, $CH{=}CH_2$), 5.76–5.98 (m, 6H, $CH{=}CH_2$); $^{13}C\{^1H\}$ NMR (100.64 MHz, $CDCl_3$): $\delta = 8.29$ [$|^1J(^{13}C^{117/119}Sn)| = 148.0/155.0$ Hz, $SnCH_2C_3H_5$], 9.37 $|^1J(^{13}C^{117/119}Sn)| = 154.0/161.0$ Hz, $CH_2SnC_4H_7$), 20.39 [$|^2J(^{13}C^{119}Sn)| = 10.1$ Hz, $CH_2CH_2SnC_4H_7$], 30.83 [$|^2J(^{13}C^{119}Sn)| = 8.9$ Hz, $SnCH_2CH_2C_2H_3$], 39.20 [$|^3J(^{13}C^{117/119}Sn)| = 25.3/26.2$ Hz, $CH_2CH_2CH_2SnC_4H_7$], 112.91 ($CH{=}CH_2$), 141.95 [$|^3J(^{13}C^{117/119}Sn)| = 24.3/25.1$ Hz, $CH{=}CH_2$]; $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): $\delta = -7.21$; MS [100 °C, m/z (%)]: 583.3 (0.3) [$M - C_4H_7]^+$, 528.1 (0.1) [$M - 2C_4H_7]^+$, 473.1 (0.1) [$M - 3C_4H_7]^+$, 419.1 (0.1) [$M - 4C_4H_7]^+$, 363.0 (0.1) [$M - 5C_4H_7]^+$, 308.0 (0.3) [$M - 6C_4H_7]^+$, 285.3 (100) [$M - C_5H_{10} - Sn - 3C_4H_7]^+$, 229.1 (8.0) [$M - C_5H_{10} - Sn - 4C_4H_7]^+$, 173.1 (8.6) [$M - C_5H_{10} - Sn - 5C_4H_7]^+$, 120.1 (1.2) $[Sn]^+$. Anal. calcd for $C_{29}H_{52}Sn_2$ (638.11 g/mol): C, 54.59; H, 8.21%. Found: C, 54.46; H, 8.13%.

*1,4-Bis[tri-(4-triphenylstannyl)butylstannyl] butane, **6a***

A 7.76 g (22.11 mmol) aliquot of freshly distilled Ph_3SnH was treated with AIBN (0.18 g, 5 mol%, 1.11 mmol) and stirred at room temperature for 0.5 h. Then 2.30 g (3.69 mmol) of **5a** were added slowly within 0.5 h. The stirring of the mixture were continued for 12 h at ambient temperature. During this time, the reaction solution changed into a viscous solid. It was dissolved in toluene (10 ml) and the solution was stirred for additional 6 h. Addition of pentane (25 ml) to the light yellow solution resulted in the formation of a white precipitate which was separated by filtration and washed several times with 25 ml of a mixture of pentane–diethyl ether (50 : 50). Removal of the solvents in vacuum (10^{-2} mbar) afforded **6a** as white viscous solid. Yield: 7.65 g (76%).

^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 0.60–0.79$ [m, 12H, $SnCH_2(CH_2)_3SnPh_3$], 1.13–1.28 [m, 8H, $(CH_2)_4Sn(CH_2)_4SnPh_3$], 1.42–1.61 [m, 24H, $SnCH_2(CH_2)_2CH_2SnPh_3$], 1.61–1.79 [m, 12H, $Sn(CH_2)_3CH_2SnPh_3$], 7.32–7.43 (m, 54H, $H^{meta/para}$), 7.52–7.65 (m, 36H, H^{ortho}); $^{13}C\{^1H\}$ NMR (100.64 MHz, $CDCl_3$): $\delta = 8.35$ [$|^1J(^{13}C^{117/119}Sn)| = 147.1/154.0$ Hz, $SnCH_2(CH_2)_3SnPh_3$], 8.93 [$(CH_2)_4Sn(CH_2)_4SnPh_3$], 10.70 [$|^1J(^{13}C^{117/119}Sn)| = 188.6/197.6$ Hz, $Sn(CH_2)_3CH_2SnPh_3$], 31.39 [$|^2J(^{13}C^{119}Sn^p)| = 9.8$ Hz, $|^3J(^{13}C^{119}Sn^z)| = 28.1$ Hz, $Sn(CH_2)_2CH_2CH_2SnPh_3$], 31.81 [$|^2J(^{13}C^{119}Sn^z)| = 9.2$ Hz, $|^3J(^{13}C^{119}Sn^p)| = 32.2$ Hz, $SnCH_2CH_2(CH_2)_2SnPh_3$], 128.42 [$|^3J(^{13}CSn)| = 23.7$ Hz, Ph-C^{meta}], 128.76 [$|^4J(^{13}CSn)| = 6.0$ Hz, Ph-C^{para}], 136.99 [$|^2J(^{13}CSn)| = 17.4$ Hz, Ph-C^{ortho}], 139.09 [$|^1J(^{13}C^{117/119}Sn)| = 229.4/240.1$ Hz, Ph-C^{ipso}]; $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): $\delta = -11.35$ (Sn^z), -99.05 (Sn^p); MS-MALDI-TOF (IAA, THF): m/z 2753.33 $[M + Na]^+$ (calcd 2753.3), 2862.6 $[M + Na + Ag]^+$ (calcd 2861.2). Anal. calcd for $C_{136}H_{146}Sn_8$ (2730.18 g/mol): C, 59.83; H, 5.39%. Found: C, 59.46; H, 5.11%.

*1,5-Bis[tri-(4-triphenylstannyl)butylstannyl] pentane, **6b***

In analogy to the synthesis of **6a**, a mixture of 7.26 g (20.68 mmol) of freshly distilled Ph_3SnH and AIBN (0.18 g, 5 mol%, 1.03 mmol) was treated with 2.20 g (3.45 mmol) of **5b**. After analogous workup, **6b** was isolated as white viscous oil. Yield: 5.68 g (60%).

^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 0.62–0.68$ [m, 4H, $CH_2Sn(CH_2)_4SnPh_3$], 0.68–0.75 [m, 12H, $SnCH_2(CH_2)_3SnPh_3$], 1.30–1.38 [m, 6H, $SnCH_2(CH_2)_3CH_2Sn(CH_2)_4SnPh_3$], 1.46–1.59 [m, 24H, $SnCH_2(CH_2)_2CH_2SnPh_3$], 1.66–1.76 [m, 12H, $Sn(CH_2)_3CH_2SnPh_3$], 7.33–7.43 (m, 54H, Ph-$H^{meta/para}$), 7.56–7.62 (m, 36H, Ph-H^{ortho}); $^{13}C\{^1H\}$ NMR (100.64 MHz, $CDCl_3$): $\delta = 8.28$ [$|^1J(^{13}C^{117/119}Sn)| = 147.3/154.3$ Hz, $SnCH_2(CH_2)_3SnPh_3$], 8.33 [$Sn(CH_2)_2CH_2(CH_2)_2Sn(CH_2)_4SnPh_3$], 10.62 [$|^1J(^{13}C^{117/119}Sn)| = 189.3/197.9$ Hz, $Sn(CH_2)_3CH_2SnPh_3$], 31.38 [$|^3J(^{13}C^{119}Sn^p)| = 34.8$ Hz, $|^2J(^{13}C^{119}Sn^z)| = 9.3$ Hz, $SnCH_2CH_2CH_2CH_2SnPh_3$], 31.78 [$|^3J(^{13}C^{119}Sn^z)| = 32.8$ Hz, $|^2J(^{13}C^{119}Sn^p)| = 9.7$ Hz, $SnCH_2CH_2CH_2CH_2SnPh_3$], 31.92 [$Sn(CH_2)_2CH_2(CH_2)_2Sn(CH_2)_4SnPh_3$], 128.44 [$|^3J(^{13}CSn)| = 23.7$ Hz, Ph-C^{meta}], 128.78 [$|^4J(^{13}CSn)| = 5.4$ Hz, Ph-C^{para}], 137.46 [$|^2J(^{13}CSn)| = 17.2$ Hz, Ph-C^{ortho}], 139.12 [$|^1J(^{13}C^{117/119}Sn)| = 229.0/239.8$ Hz, Ph-C^{ipso}]; $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): $\delta = -11.58$ (Sn^z), -99.07 (Sn^p); MS-MALDI-TOF (IAA, THF): m/z 2767.35 $[M + Na]^+$ (calcd 2767.4), 2875.3 $[M + Na + Ag]^+$ (calcd 2875.2). Anal. calcd for $C_{137}H_{148}Sn_8$ (2744.20 g/mol): C, 59.96; H, 5.44%. Found: C, 59.59; H, 5.27%.

*1,4-Bis[tri-(4-chlorodiphenylstannyl) butylstannyl]butane, **7a***

To a vigorously stirred solution of **6a** (4.94 g, 1.81 mmol) in CH_2Cl_2 (50 ml), which was cooled down to −78 °C, 5.87 ml (10.86 mmol) of a 1.85 M solution of anhydrous HCl(g) in diethyl ether were added dropwise within 1 h. The mixture was stirred at −78 °C for 5 h, then it was allowed to warm up gradually to room temperature. After stirring for further 12 h, the solvents and the benzene formed in the reaction were removed in vacuum (10^{-2} mbar), leaving **7a** as light yellow viscous oil. Yield: 4. 26 g (95%).

^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 0.70–0.89$ [m, 12H, $SnCH_2(CH_2)_3SnCl$], 1.14–1.49 [m, 8H, $(CH_2)_4Sn(CH_2)_4SnCl$], 1.52–1.67 [m, 12H, $Sn(CH_2)_3CH_2SnCl$], 1.73–1.88 [m, 24H, $SnCH_2(CH_2)_2CH_2SnCl$], 7.60–7.69 (m, 24H, Ph-H^{ortho}), 7.40–7.55 (m, 36H, Ph-$H^{meta/para}$); $^{13}C\{^1H\}$ NMR (100.64 MHz, $CDCl_3$): $\delta = 8.29$ [$|^1J(^{13}C^{117/119}Sn)| = 146.1/156.1$ Hz, $SnCH_2(CH_2)_3SnCl$], 8.49 [$|^1J(^{13}C^{117/119}Sn)| = 136.5/146.1$ Hz, $CH_2Sn(CH_2)_4SnCl$], 17.07 [$|^1J(^{13}C^{117/119}Sn)| = 203.0/212.3$ Hz, $Sn(CH_2)_3CH_2SnCl$], 29.64 [$SnCH_2(CH_2)_2CH_2Sn(CH_2)_4SnCl$],

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30.15 [$|^2J(^{13}C^{119}Sn^z)| = 13.9$ Hz, $|^3J(^{13}C^{119}Sn^p)| = 40.3$ Hz, $SnCH_2CH_2(CH_2)_2SnCl$], 31.13 [$|^2J(^{13}C^{119}Sn^p)| = 15.0$ Hz, $|^3J(^{13}C^{119}Sn^z)| = 37.9$ Hz, $Sn(CH_2)_2CH_2CH_2SnCl$], 128.91 [$|^3J(^{13}C^{119}Sn)| = 27.8$ Hz, Ph-C^{meta}], 130.07 [$|^4J(^{13}C^{119}Sn)| = 5.6$ Hz, Ph-C^{para}], 135.72 [$|^2J(^{13}C^{119}Sn)| = 23.7$ Hz, Ph-C^{ortho}], 139.98 [$|^1J(^{13}C^{117/119}Sn)| = 256.7/268.7$ Hz, Ph-C^{ipso}]; $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): $\delta = -10.75$ (Sn^z), 17.10 (Sn^p); MS-MALDI-TOF (IAA, THF): m/z 2503.45 $[M + Na]^+$ (calcd 2539.3), 2519.30 $[M + K]^+$ (calcd 2519.40), 2565.20 $[M + 2Na + K]^+$ (calcd 2565.40). Anal. calcd for $C_{100}H_{116}Cl_6Sn_8$ (2480.26 g/mol): C, 48.43; H, 4.71%. Found: C, 48.09; H, 4.33%.

1,5-Bis[tri-(4-chlorodiphenylstannyl) butylstannyl]pentane, ***7b***

In analogy to the synthesis of **7a**, the addition of 5.15 ml (9.53 mmol) of a 1.85 M solution of anhydrous HCl(g) in diethyl ether to a solution of 4.36 g (1.59 mmol) of **6b** in CH_2Cl_2 (50 ml) resulted in the formation of **7b** which was isolated as yellowish viscous oil. Yield: 3.61 g (91%).

^1H NMR (400.13 MHz, $CDCl_3$): δ 0.61–0.82 [m, 12H, $SnCH_2(CH_2)_3SnCl$], 1.14–1.25 [m, 4H, $CH_2Sn(CH_2)_4SnCl$], 1.33–1.42 [m, 6H, $SnCH_2(CH_2)_3CH_2Sn(CH_2)_4SnCl$], 1.46–1.60 [m, 12H, $Sn(CH_2)_3CH_2SnCl$], 1.66–1.81 [m, 24H, $SnCH_2(CH_2)_2CH_2SnCl$], 7.36–7.45 (m, 36H, Ph-$H^{meta/para}$), 7.53–7.63 (m, 24H, Ph-H^{ortho}); $^{13}C\{^1H\}$ NMR (100.64 MHz, $CDCl_3$): $\delta =$ 8.26 [$|^1J(^{13}C^{117/119}Sn)| = 147.3/154.3$ Hz, $SnCH_2(CH_2)_3SnCl$], 8.46 [$CH_2Sn(CH_2)_4SnCl$], 17.07 [$|^1J(^{13}C^{117/119}Sn)| = 203.2/212.4$ Hz, $Sn(CH_2)_3CH_2SnCl$], 29.64 [$SnCH_2(CH_2)_3CH_2Sn(CH_2)_4SnCl$], 31.03 [$|^2J(^{13}C^{119}Sn^p)| = 14.6$ Hz, $|^3J(^{13}C^{119}Sn^z)| = 40.8$ Hz, $Sn(CH_2)_2CH_2CH_2SnCl$], 31.92 [$|^2J(^{13}C^{119}Sn^z)| = 14.0$ Hz, $|^3J(^{13}C^{119}Sn^p)| = 42.9$ Hz, $SnCH_2CH_2(CH_2)_2SnCl$], 128.99 [$|^3J(^{13}C^{119}Sn)| = 28.5$ Hz, Ph-C^{meta}], 130.15 [$|^4J(^{13}C^{119}Sn)| = 5.6$ Hz, Ph-C^{para}], 135.83 [$|^2J(^{13}C^{119}Sn)| = 24.2$ Hz, Ph-C^{ortho}], 139.08 [$|^1J(^{13}C^{117/119}Sn)| = 256.5/268.8$ Hz, Ph-C^{ipso}]; $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): $\delta = -11.01$ (Sn^z), 17.32 (Sn^p); MS-MALDI-TOF (IAA, THF): m/z 2493.57 $[M]^+$ (calcd 2494.41), 2602.2 $[M + Ag]^+$ (calcd 2602.3). Anal. calcd for $C_{101}H_{118}Cl_6Sn_8$ (2494.29 g/mol): C, 48.64; H, 4.77%. Found: C, 48.17; H, 4.24%.

1,4-Bis[tri-(4-hydridodiphenylstannyl) butylstannyl]butane, ***8a***

A solution of **7a** (3.75 g, 1.51 mmol) in diethyl ether (100 ml) was added dropwise to a suspension of $LiAlH_4$ (0.27 g, 7.1 mmol) in diethyl ether (100 ml) at 0 °C within 1 h. The resulting brown solution was stirred for 1 h at this temperature and 5 h at room temperature and was then hydrolyzed carefully at 0 °C using a mixture of water (0.13 g, 7.2 mmol) in dioxan (20 ml). After stirring for 0.5 h at room temperature, the solid reaction products were filtered off and extracted three times with diethyl ether (25 ml). The combined organic fractions were washed twice with a saturated aqueous solution of NH_4Cl (20 ml) and twice with a saturated aqueous solution of NaCl (20 ml) and then dried with Na_2SO_4. After evaporation of the solvents in vacuum (10^{-2} mbar), **8a** was isolated as colorless viscous oil. Yield: 3.33 g (97%).

IR (KBr, film): ν (Sn–H) 1830 cm^{-1} (s); ^1H NMR (400.13 MHz, C_6D_6): $\delta = 0.80–0.92$ [m, 12H, $SnCH_2(CH_2)_3SnH$], 0.93–0.99 [m, 4H, $CH_2Sn(CH_2)_4SnH$], 1.15–1.23 [m, 4H, $Sn[CH_2(CH_2)_2CH_2Sn(CH_2)_4SnH]$, 1.28–1.42 [m, 12H, $Sn(CH_2)_2CH_2SnH$], 1.53–1.80 [m, 24H, $SnCH_2(CH_2)_2CH_2SnH$], 6.39 [s, 6H, $|^2J(^1H^{117/119}Sn)| = 862.2/902.2$ Hz, SnH], 7.11–7.25 (m, 36H, Ph-$H^{meta/para}$), 7.51–7.58 (m, 24H, Ph-H^{ortho}); $^{13}C\{^1H\}$ NMR (100.64 MHz, C_6D_6): $\delta = 8.50$ [$|^1J(^{13}C^{117/119}Sn)| = 115.5/119.6$ Hz, $CH_2Sn(CH_2)_4SnH$], 8.91 [$|^1J(^{13}C^{117/119}Sn)| = 147.7/154.5$ Hz, $SnCH_2(CH_2)_3SnH$], 9.10 [$|^2J(^{13}C^{119}Sn)| = 9.5$ Hz, $SnCH_2(CH_2)_2CH_2Sn(CH_2)_4SnH$], 10.26 [$|^1J(^{13}C^{117/119}Sn)| = 188.3/197.0$ Hz, $Sn(CH_2)_3CH_2SnH$], 31.92 [$|^2J(^{13}C^{119}Sn^z)| = 9.6$ Hz, $|^3J(^{13}C^{119}Sn^p)| = 29.32$ Hz, $SnCH_2CH_2(CH_2)_2SnH$], 32.24 [$|^2J(^{13}C^{119}Sn^p)| = 11.8$ Hz, $|^3J(^{13}C^{119}\ Sn^z)| = 26.3$ Hz, $Sn(CH_2)_2CH_2CH_2SnH$], 128.83 [$|^3J(^{13}C^{119}Sn)| = 23.6$ Hz, Ph-C^{meta}], 129.05 [$|^4J(^{13}C^{119}Sn)| = 5.7$ Hz, Ph-C^{para}], 137.51 [$|^2J(^{13}C^{119}Sn)| = 18.3$ Hz, Ph-C^{ortho}], 138.30 [$|^1J(^{13}C^{117/119}Sn)| = 233.0/243.9$ Hz, Ph-C^{ipso}]; $^{119}Sn\{^1H\}$ NMR (149.21 MHz, C_6D_6): $\delta = -11.99$ (Sn^z), −136.63 (Sn^p); MS-MALDI-TOF (IAA, THF): m/z 2313.53 $[M + K]^+$ (calcd 2312.7), 2337.72 $[M + Na + K]^+$ (calcd 2335.72). Anal. calcd for $C_{100}H_{122}Sn_8$ (2273.59 g/mol): C, 52.83; H, 5.41. Found: C, 52.74; H, 5.29%.

1,5-Bis[tri-(4-hydridodiphenylstannyl) butylstannyl]pentane, ***8b***

In analogy to the synthesis of **8a,** a suspension of $LiAlH_4$ (0.18 g, 4.74 mmol) in diethyl ether (100 ml) was treated with a solution of **7b** (2.50 g, 1.0 mmol) in diethyl ether (100 ml). After analogous workup, **8b** was isolated as colorless viscous oil. Yield: 2.26 g (99%). IR (KBr, film): ν (Sn–H) 1829 cm^{-1} (s); ^1H NMR (400.13 MHz, C_6D_6): $\delta = 0.79–0.90$ [m, 12H, $SnCH_2(CH_2)_3SnH$], 0.91–0.97 [m, 8H, $Sn(CH_2)_2CH_2(CH_2)_2Sn(CH_2)_4SnH$], 1.14–1.22 [m, 2H, $Sn(CH_2)_2CH_2(CH_2)_2Sn(CH_2)_4SnH$], 1.28–1.40 [m, 12H, $Sn(CH_2)_3CH_2SnH$], 1.50–1.81 [m, 24H, $SnCH_2(CH_2)_2CH_2SnH$], 6.38 [s, $|^2J(^1H^{117/119}Sn)| = 862.0/902.0$ Hz, SnH], 7.15–7.21 (m, 36H, Ph-$H^{meta/para}$), 7.52–7.58 (m, 24H, Ph-H^{ortho}); $^{13}C\{^1H\}$ NMR (100.64 MHz, C_6D_6): $\delta = 8.50$ [$|^1J(^{13}C^{117/119}Sn)| = 115.0/119.9$ Hz, $Sn(CH_2(CH_2)_3CH_2Sn(CH_2)_4SnH]$, 8.88 [$|^1J(^{13}C^{117/119}Sn)| = 147.4/154.2$ Hz, $SnCH_2(CH_2)_3SnH$], 9.49 [$|^2J(^{13}C^{117/119}Sn)| = 27.0/32.2$ Hz, $SnCH_2CH_2CH_2CH_2CH_2Sn(CH_2)_4SnH$], 10.26 [$|^1J(^{13}C^{117/119}Sn)| = 188.6/197.3$ Hz, $Sn(CH_2)_3CH_2SnH$], 27.25 [$Sn(CH_2)_2CH_2(CH_2)_2Sn(CH_2)_4SnH$], 31.89 [$|^2J(^{13}C^{119}Sn^z)| = 9.5$ Hz, $|^3J(^{13}C^{119}Sn^p)| = 30.0$ Hz $SnCH_2CH_2(CH_2)_2SnH$], 32.20 [$|^2J(^{13}C^{119}Sn^p)| = 11.4$ Hz, $|^3J(^{13}C^{119}\ Sn^z)| = 26.7$ Hz, $Sn(CH_2)_2CH_2CH_2SnH$], 128.83 [$|^3J(^{13}C^{119}Sn)| = 23.9$ Hz, Ph-C^{meta}], 129.05 ($|^4J(^{13}C^{119}Sn)| = 5.5$ Hz, Ph-C^{para}], 137.51 [$|^2J(^{13}C^{119}Sn)| = 18.2$ Hz, Ph-C^{ortho}], 138.30 [$|^1J(^{13}C^{117/119}Sn)| = 233.0/243.6$ Hz, Ph-C^{ipso}]; $^{119}Sn\{^1H\}$ NMR (149.21 MHz, C_6D_6): $\delta = -11.55$ (Sn^z), −136.52 (Sn^p); MS-MALDI-TOF (IAA, THF): m/z 2311.8 $[M + Na]^+$ (calcd 2311.2), 2336.79

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$[M + 2Na]^+$ (calcd 2334.2). Anal. calcd for $C_{101}H_{124}Sn_8$ (2287.62 g/mol): C, 53.03; H, 5.46. Found: C, 52.86; H, 5.24%.

*1,4-Bis[tri-4-(3-hydroxipropyl) diphenylstannylbutylstannyl]butane, **9a***

To a mixture of **8a** (1.27 g, 0.56 mmol) and AIBN (4.6 mg, 0.03mmol) in toluene (5 ml) a solution of CH_2=$CHCH_2OH$ (195.15 mg, 3.36 mmol) in toluene (5 ml) was added dropwise at 0 °C within 1 h. The resulting solution was kept for 24 h at room temperature. After removal of the solvents and unreacted CH_2=$CHCH_2OH$ in vacuum (10^{-2} mbar), **9a** was isolated as colorless viscous oil. Yield: 1.42 g (97%).

IR (KBr, film): ν (OH) 3345 cm^{-1} (s); ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 0.61–0.81$ [m, 16H, $Sn(CH_2(CH_2)_2CH_2SnCH_2(CH_2)_3SnPh_2R]$, 1.18–1.40 [m, 12H, $Sn(CH_2)_3CH_2SnPh_2R]$, 1.42–1.67 [m, 28H, $SnCH_2(CH_2)_2CH_2SnCH_2CH_2CH_2CH_2SnPh_2R]$, 1.56 (t, $J = 6.9$ Hz, 12H, $SnPh_2(CH_2CH_2CH_2OH)$, 1.77 (s, 6H, OH), 1.85–1.92 [m, 12H, $SnPh_2(CH_2CH_2CH_2OH)$], 3.52 [m, 12H, $SnPh_2(CH_2CH_2CH_2OH)$], 7.23–7.43 (m, 36H, Ph-$H^{meta/para}$), 7.45–7.57 (m, 24H, Ph-H^{ortho}); $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): $\delta = 5.87$ [$|^1J(^{13}C^{117/119}Sn)| =$ 173.3/181.2 Hz, $SnPh_2(CH_2CH_2CH_2OH)$], 8.46 [$|^1J(^{13}C^{117/119}Sn)| = 147.7/155.3$ Hz, $SnCH_2(CH_2)_3SnPh_2R]$, 9.00 [$SnCH_2(CH_2)_2CH_2Sn(CH_2)_4SnPh_2R]$, 10.19 [$|^1J(^{13}C^{117/119}Sn)| = 178.2/186.7$ Hz, $Sn(CH_2)_3CH_2SnPh_2R]$, 26.63 [$SnCH_2(CH_2)CH_2Sn(CH_2)_4SnPh_2R]$, 29.48 [$|^2J(^{13}C^{119}Sn^z)| = 9.8$ Hz, $SnPh_2(CH_2CH_2CH_2OH)$), 31.50 [$|^2J(^{13}C^{119}Sn^p)| = 11.2$ Hz, $|^3J(^{13}C^{119}Sn^z)| = 27.5$ Hz, $Sn(CH_2)_2CH_2CH_2SnPh_2R]$, 31.83 [$|^2J(^{13}C^{/119}Sn^z)| = 9.3$ Hz, $|^3J(^{13}C^{119}Sn^p)| = 40.1$ Hz, $SnCH_2CH_2(CH_2)_2SnPh_2R]$, 65.70 [$|^3J(^{13}C^{119}Sn^p)| = 32.4$ Hz, $SnPh_2(CH_2CH_2CH_2OH)$], 128.24 [$|^3J(^{13}C^{119}Sn)| = 22.3$ Hz, Ph-C^{meta}], 128.44 [$|^4J(^{13}C^{119}Sn)| = 4.6$ Hz, Ph-C^{para}], 136.68 [$|^2J(^{13}C^{119}Sn)| = 16.9$ Hz, Ph-C^{ortho}], 140.11 [$|^1J(^{13}C^{117/119}Sn)| =$ 211.0/220.7 Hz, Ph-C^{ipso}]; $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): $\delta = -11.69$ (Sn^z), -70.26 (Sn^p); MS-MALDI-TOF (IAA, THF): m/z 2647.3 $[M + Na]^+$ (calcd 2645.43), 2565.1 $[M - C_3H_6OH]^+$ (calcd 2663.19), 2487.51 $[M - C_3H_6OH - C_6H_5]^+$ (calcd 2486.19). Anal. calcd for $C_{118}H_{158}O_6Sn_8$ (2622.07 g/mol): C, 54.05; H, 6.07. Found: C, 53.74; H, 5.59%.

*1,5-Bis[tri-{4-(3-hydroxipropyl) diphenylstannyl}butylstannyl]pentane, **9b***

In analogy to the synthesis of **9a**, a toluene solution of **8b** (1.12 g, 0.49 mmol) and AIBN (4.07 mg, 0.024 mmol) was treated with a toluene solution of CH_2=$CHCH_2OH$ (170.75 mg, 2.94 mmol). After analogous workup, **9b** was isolated as colorless viscous oil. Yield: 1.28 g (99%).

IR (KBr, film): ν (OH) 3367 cm^{-1} (s); ^1H NMR (200.13 MHz, $CDCl_3$): $\delta = 0.61–0.84$ [m, 16H, $SnCH_2(CH_2)_3CH_2SnCH_2(CH_2)_3SnPh_2R]$, 1.19–1.41 [m, 12H, $Sn(CH_2)_3CH_2SnPh_2R]$, 1.43–1.68 [m, 30H, $SnCH_2(CH_2)_3CH_2SnCH_2(CH_2)_2CH_2SnPh_2R]$, 1.54 [t, 12H, $J = 6.9$ Hz, $SnPh_2(CH_2CH_2CH_2OH)$], 1.77 (s, 6H, OH), 1.79–1.94 [m, 12H, $SnPh_2(CH_2CH_2CH_2OH)$], 3.49–3.62 [m, 12H, $SnPh_2(CH_2CH_2CH_2OH)$], 7.28–7.47 (m, 36H, P-$H^{meta/para}$), 7.47–7.57 (m, 24H, Ph-H^{ortho}); $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): $\delta = 5.87$ [$|^1J(^{13}C^{117/119}Sn)| =$ 173.3/181.2 Hz, $SnPh_2(CH_2CH_2CH_2OH)$], 8.47 [$|^1J(^{13}C^{117/119}Sn)| = 148.8/155.9$ Hz, $SnCH_2(CH_2)_3SnPh_2R]$, 8.61 [$SnCH_2(CH_2)_3CH_2Sn(CH_2)_4SnPh_2R]$, 10.18 [$|^1J(^{13}C^{117/119}Sn)| = 178.5/186.7$ Hz, $Sn(CH_2)_3CH_2SnPh_2R]$, 23.39 [$Sn(CH_2)_2CH_2(CH_2)_2Sn(CH_2)_4SnPh_2R]$, 25.09 [$SnCH_2CH_2CH_2CH_2CH_2Sn(CH_2)_4SnPh_2R]$, 29.48 [$|^2J(^{13}C^{119}Sn)| = 9.8$ Hz, $SnPh_2(CH_2CH_2CH_2OH)$], 31.51 [$|^2J(^{13}C^{119}Sn^p)| = 12.8$ Hz, $|^3J(^{13}C^{119}Sn^z)| = 27.1$ Hz, $Sn(CH_2)_2CH_2CH_2SnPh_2R]$, 31.84 [$|^2J(^{13}C^{119}Sn^z)| = 8.5$ Hz, $|^3J(^{13}C^{119}Sn^p)| = 44.4$ Hz, $SnCH_2CH_2(CH_2)_2SnPh_2R]$, 65.68 [$|^3J(^{13}C^{119}Sn)| = 32.4$ Hz, $SnPh_2(CH_2CH_2CH_2OH)$], 128.24 [$|^3J(^{13}C^{119}Sn)| = 22.3$ Hz, Ph-C^{meta}], 128.44 [$|^4J(^{13}C^{119}Sn)| = 4.6$ Hz, Ph-C^{para}], 136.68 [$|^2J(^{13}C^{119}Sn)| = 16.9$ Hz, Ph-C^{ortho}], 140.12 [$|^1J(^{13}C^{117/119}Sn)| =$ 210.6/220.4 Hz, C^{ipso}]; $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$): $\delta = -11.45$ (Sn^z), -70.28 (Sn^p); MS-MALDI-TOF (IAA, THF): m/z 2659.5 $[M + Na]^+$ (calcd 2659.22). Anal. calcd for $C_{119}H_{160}O_6Sn_8$ (2636.10 g/mol): C, 54.22; H, 6.12. Found: C, 53.79; H, 5.94%.

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REFERENCES

1. Gorman C. *Adv. Mater.* 1998; **10**: 295.
2. Newcome GR, He E, Moorefield CN. *Chem. Rev.* 1999; **99**: 1.
3. Zeng F; Zimmerman SC. *Chem. Rev.* 1997; **97**: 1681.
4. Hecht S, Fréchet JMJ. *Angew. Chem.* 2001; **113**: 76.
5. Hecht S, Fréchet JMJ. *Angew. Chem. Int. Edn Engl.* 2001; **40**: 74.
6. Achar S, Puddephatt J. *Organometallics* 1995; **14**: 1681.
7. Stebani U, Lattermann G, Wittenberg M, Wendorff JH. *Angew. Chem.* 1996; **108**: 1941.
8. Stebani U, Lattermann G, Wittenberg M, Wendorff JH. *Angew. Chem. Int. Edn Engl.* 1996; **35**: 1858.
9. Balzani V, Campagna S, Denti G, Juris A, Serroni S, Venturi M. *Acc. Chem. Res.* 1998; **31**: 26.
10. Reetz MT, Giebel D. *Angew. Chem.* 2000; **112**: 2614.
11. Reetz MT, Giebel D. *Angew. Chem. Int. Edn Engl.* 2000; **39**: 2498.
12. Lang H, Lühmann B. *Adv. Mater.* 2001; **13**: 1523.
13. Beer PD, Kocian O, Mortimer RJ, Ridgway C. *J. Chem. Soc. Chem. Commun.* 1991; 1460.
14. Nagasaki T, Kimura O, Ukon M, Arimori S, Hamachi I, Shinkai S. *J. Chem. Soc. Perkin Trans. 1* 1994; 75.
15. Bochkarev MN, Katkova M. *Usp. Khim.* 1995; **64**: 1106.
16. Bochkarev MN, Katkova M. *Russ. Chem. Rev.* 1995; **64**: 1034.
17. Huc V, Boussaguet P, Mazerolles P. *J. Organomet. Chem.* 1996; **521**: 253.
18. Suzuki H, Kurata H, Matano Y. *Chem. Commun.* 1997; 2295.
19. Majoral AM, Caminade A. *Chem. Rev.* 1999; **99**: 845.
20. Semchikov YuD, Bochkarev MN. *Vysokomol. Soedin. Ser. C* 2002; **44**: 2293.
21. Semchikov YuD, Bochkarev MN. *Polym. Sci. C.* 2002; **44**(2): 143.
22. Pestova II, Khanov EN, Kulikova TI, Kurskii YuA, Khorshev SYa, Mushtina TG, Zaitsev SD, Semchikov YuD, Bochkarev MN. *Vysokomol. Soedin. Ser. B* 2004; **46**: 1438.
23. Pestova II, Khanov EN, Kulikova TI, Kurskii YuA, Khorshev SYa, Mushtina TG, Zaitsev SD, Semchikov YuD, Bochkarev MN. *Polymer Sci. B* 2004; **46**(7–8): 237.
24. Schumann H, Wassermann BC, Frackowiak M, Omotowa B, Schutte S, Velder J, Mühle SH, Krause W. *J. Organomet. Chem.* 2000; **609**: 189.

25. Schumann H, Wassermann BC, Schutte S, Velder J, Aksu Y, Krause W, Radüchel B. *Organometallics* 2003; **22**: 2034.
26. Schumann H, Aksu Y, Wassermann BC. *J. Organomet. Chem.* 2006; **691**: 1703.
27. Schumann H, Aksu Y, Wassermann BC. *Organometallics* 2006; **25**: 3428.
28. Schumann H, Aksu Y, Schutte S, Wassermann BC, Mühle SH. *J. Organomet. Chem.* 2006; **691**: 4717.
29. Schumann H, Aksu Y. *Organometallics* 2007; **26**: 397.
30. Krause W, Schumann H. (Schering AG, Germany) German Patent DE 197 26 340, 1999 [*Chem. Abstr.* 1998; **128**: 180522.].
31. Kraus CA, Neal AM. *J. Am. Chem. Soc.* 1930; **52**: 695.
32. Kraus CA, Sessions WV. *J. Am. Chem. Soc.* 1925; **47**: 2361.
33. Zobel B, Duthie A, Dakternieks D, Tiekink ERT. *Organometallics* 2001; **20**: 2820.
34. Jousseaume B, Riague H, Toupance T, Lahcini M, Mountford P, Tyrrell BR. *Organometallics* 2002; **21**: 4590.
35. Gielen M, De Porter B, Liberton R, Paelinck MT. *Bull. Soc. Chim. Belges* 1973; **82**: 277.
36. Kauffmann T, Kriegesmann R, Altepeter B, Steinseifer F. *Chem. Ber.* 1982; **115**: 1810.
37. Gilman H, Eisch J. *J. Org. Chem.* 1955; **20**: 763.
38. Zimmer H, Moslé HG. *Chem. Ber.* 1954; **87**: 1255.
39. Newcomb M, Azuma Y, Courtney AR. *Organometallics* 1983; **2**: 175.
40. Gielen M, Jurkschat K. *Org. Mass Spectry.* 1983; **18**: 224.
41. Azuma Y, Newcomb M. *Organometallics* 1984; **3**: 9.
42. Carré F, Dutremez SG, Guérin C, Henner BJL, Jolivet A, Tomberli V. *Organometallics* 1999; **18**: 770.
43. Zimmer H, Miller J. *Naturwissenschaften* 1966; **53**: 38.
44. Dakternieks D, Duthie A, Jurkschat K, Schurmann M, Tiekink ERT. *Main Group Metal Chem.* 2002; **25**: 73.
45. Van der Kerk GJM, Noltes JG, Luijten JGA. *J. Appl. Chem.* 1957; **7**: 366.

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