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# Synthesis and characterization of some organo-all-tin dendrimers with different peripheral substituents

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**Abstract**

The synthesis of the first all-tin-dendrimer $Sn[(CH_2)_4SnPh_3]_4$ (**2**) results from complete hydrostannation of tetra(but-3-enyl)stannane (**1**) with triphenyltin hydride. Selective cleavage of one phenyl group from each dendron of **2** with anhydrous HCl results in $Sn[(CH_2)_4Sn(Cl)Ph_2]_4$ (**3**), which on treatment with $LiAlH_4$ yields the corresponding hydride derivative $Sn[(CH_2)_4Sn(H)Ph_2]_4$ (**4**) containing four reactive Sn–H bonds. The cyclopentadienyl derivative $Sn[(CH_2)_4Sn(C_5H_5)Ph_2]_4$ (**5**) as well as the transition metal substituted derivatives $Sn[(CH_2)_4Sn\{Co(CO)_4\}Ph_2]_4$ (**6**), $Sn[(CH_2)_4Sn\{Fe(CO)_2C_5H_5\}Ph_2]_4$ (**7**), and $Sn[(CH_2)_4Sn\{Mn(CO)_5\}Ph_2]_4$ (**8**) have been prepared by coupling of **3** with the appropriate Grignard or sodium derivatives of the transition metal moieties. The new compounds were characterized by elemental analyses, IR, $^1$H-, $^{13}$C- and $^{119}$Sn NMR spectroscopy and MALDI-TOF mass spectrometry.


*Keywords:* Organotin compounds; Dendrimers; Organotin hydride; Iron; Cobalt; Manganese

## 1. Introduction

One of the most remarkable classes of organic compounds developed in recent years is that of dendrimers [1–3]. Due to their attractive and unique properties [4–6], as well as their diverse and promising applications for example in catalysis [7], medicine [8,9], material sciences [10], or host–guest chemistry [11], interest in this new area of chemistry increased rapidly. A rising demand for materials with novel properties forced researchers to incorporate metal atoms into different sites of the dendritic structure, creating a new class of compounds, the so-called metallodendrimers. As a result, several new dendritic systems based on metal atoms have been described during recent years [12]. Most of them consist of transition metal as well as lanthanide [13] complexes linked through coordination in the core or to the surface. Metallodendrimers containing main group metals, exclusively those, in which the metal atoms are able to occupy all branching positions in the structure, attracted considerable interest and have also been subject of several publications [14,15]. Although a few triorganotin derivatives which can be classified as dendrimers have already been described, they have not been prepared under the perspective of dendrimer synthesis, but studied in relation to multinuclear NMR spectroscopic investigations [16]. In preceding papers [17,18] we reported on the synthesis of tin containing metallodendrimers and their functionalization with water-soluble ligands with regard to application as X-ray contrast agents. Continuing our interest in organotin dendrimers we report here the synthesis and spectroscopic characterization of dendrimers with tin atoms as branching units, which can be used as suitable starting materials for new dendritic organotin macromolecules with reactive units on the periphery because they permit multiple possibilities for derivatization.

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## 2. Results and discussion

### 2.1. Synthesis of dendritic organotin compounds 2, 3, 4 and 5

Treatment of tetravinylstannane with an excess of triphenylstannane in the presence of azo-isobutyronitrile, AIBN, provided after workup of the very viscous reaction mixture with pentane a light yellow solid, whose constitution did not match that of the desired tetrakis(2-triphenylethyl)stannane, but that of 1,2-bis(triphenylstannyl)ethane [19] (Scheme 1). Variation of the reaction conditions, such as lower or higher reaction temperature, use of different solvents, changing the stoichiometry or activation by other catalysts, did not result in the formation of even traces of the dendrimer. The formation of $Ph_3SnCH_2CH_2SnPh_3$ results obviously from the reaction of triphenyltin hydride with the intermediate triphenylvinyltin already formed by vinyl/hydrogen exchange. A similar ligand redistribution process has previously been observed for the hydrostannation of diphenyldivinylstannane [20].

Tetraallylstannane reacts in the same way, forming 1,3-bis(triphenylstannyl)propane [21] and not the desired tetrakis(3-triphenylpropyl)stannane. In contrast, hydrostannation of tetrabutenylstannane (**1**) [22] succeeded, resulting in the formation of tetrakis(4-triphenylstannylbutyl)stannane (**2**), which could be isolated after 24 h stirring of a mixture of **1** and a fourfold amount of $Ph_3SnH$ in 94% yield (Scheme 1).

The addition reaction exclusively follows the anti-Markownikow rule forming exclusively $Sn[(CH_2)_4SnPh_3]_4$ (**2**) as a white solid, which is stable against moisture and air in the solid state as well as in solution. All attempts failed to get it in a crystalline state, useful for X-ray diffraction studies. Compound **2** melts at 151 °C without decomposition, and it is soluble in aromatic hydrocarbons and $CHCl_3$, but insoluble in diethyl ether and aliphatic hydrocarbons.

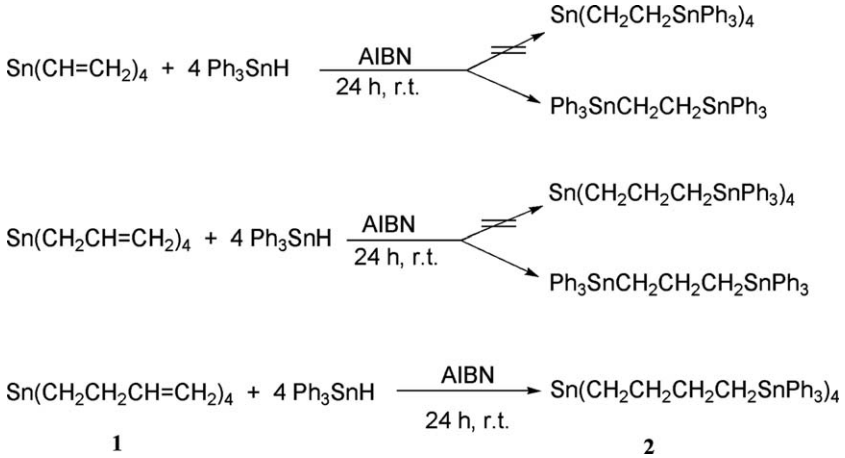
Substitution of all phenyl groups in **2** by halogens should open the way to the synthesis of second generation tin centered dendrimers. But in contrast to the well known fact, that halogens, hydrogen halides as well as some metal halides split bonds between tin and aromatic hydrocarbon ligands preferably to bonds between tin and aliphatic ligands, converting organotin compounds into their corresponding halogen derivatives [23], treatment of **2** neither with $Br_2$ nor with excess amounts of gaseous HCl in diethyl ether did not result in a complete transformation of **2** into $Sn(CH_2CH_2CH_2CH_2SnX_3)_4$. The resulting mixture of compounds containing all sorts of $-SnPh_{3-n}Cl_n$ peripheral substituents could not be separated. But reaction of **2** in $CH_2Cl_2$ at −78 °C with a little bit more than four equivalents of gaseous HCl dissolved in diethyl ether yields tetrakis[4-(chlorodiphenylstannyl)butyl]stannane (**3**) as a light yellow oil in nearly quantitative yield (Scheme 2). Crystallization of **3** was not possible, even after careful recrystallization experiments.

Due to their high reactivity, organotin hydrides represent a very important category of compounds. Treatment of **3** with $LiAlH_4$ in diethyl ether at 0 °C afforded after hydrolysis of the reaction mixture with water and subsequent workup with aqueous ammonium chloride, the hydride derivative tetrakis[4-(hydridodiphenylstannyl)butyl]stannane (**4**) as a colorless, viscous oil in 93% yield (Scheme 2). The substitution of Cl by H increased the solubility of **3** in diethyl ether in comparison to that of **1** and **2**, but the stability against water and air decreased in the same direction. Compound **4** is a powerful reagent to convert alkyl halides to the corresponding alkanes, which could be demonstrated by the NMR-monitored rapid reaction with $CHCl_3$ yielding $CH_2Cl_2$ and **3** within a few minutes.

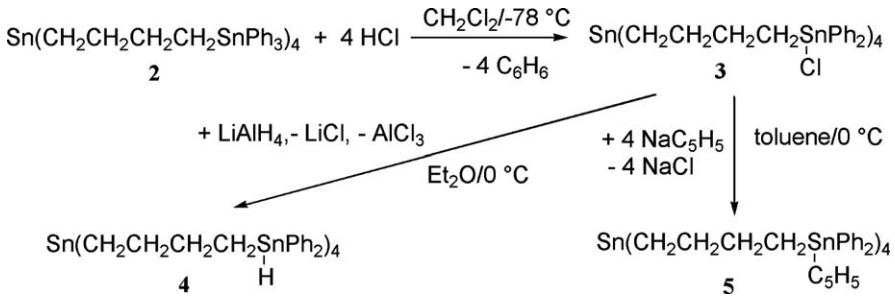
Compound **3** reacts with four equivalents of $NaC_5H_5$ in toluene with formation of tetrakis[4-(cyclopentadienyldiphenylstannyl)butyl]stannane (**5**) in 72% yield as a viscous yellow–green oil (Scheme 2), which decomposed rapidly at room temperature. However, it is considerably stable below 0 °C and can be used as a starting material for novel transition metal containing organotin dendrimers.

### 2.2. NMR and MALDI-TOF spectra of 2, 3, 4, and 5

Low intensities and overlapping of the broad $^1H$ NMR signals in the spectra of **2**, **3** and **4** prevented in most cases




Scheme 1.




Scheme 2.

the recognition of the tin hydrogen coupling constants. The $^{1}$H NMR spectrum of **2** shows two clearly separated signal ranges, two multiplets of the phenyl groups in the aromatic region and three multiplet signals between 0.45 and 1.76 ppm for the remaining aliphatic hydrogens of the butyl chain. The absence of any peaks in the olefinic region reveals the successful and complete hydrostannation. Compounds **3** and **4** exhibit similar signal patterns to **2**; the chlorine substituents in **3** shift the signals for the aliphatic protons slightly downfield, the hydrido ligands in **4** cause a weak upfield shift of those resonances. Compound **4** shows an intense singlet signal at $\delta$ 6.37 ppm for the Sn–H resonance. The large coupling constant $^{1}J(^{1}H^{117/119}Sn)$ of 1723.17/1803.76 Hz corresponds to that of $Ph_3SnH$ [24]. The $^{1}$H NMR spectrum of **5** shows only one sharp singlet with satellites caused by the coupling with $^{117/119}$Sn ($^{2}J = 22.60/23.64$ Hz) for the cyclopentadienyl protons at 6.28 ppm, illustrating the non-rigid behavior of the cyclopentadienyl group bonded to tin [25].

The $^{13}C\{^{1}H\}$ NMR spectra of **2**, **3**, **4** and **5** display distinguishable signals surrounded with Sn satellites for each carbon atom and confirm the $^{1}$H NMR results. Neither traces of olefinic resonances nor doubled signals due to non-equivalence of the dendritic branches could be observed. The $^{13}C\{^{1}H\}$ NMR spectrum of **2** shows eight well separated singlets; four for the aromatic and four for the aliphatic carbon atoms. In principle, the relation $^{1}J > {}^{3}J > {}^{2}J > {}^{4}J$ valid for the tin carbon coupling constants of most alkyl and aryl substituted tin compounds [26] permits an exact assignment of all signals. Thus, the two upfield resonances at 8.32 and 10.69 ppm have been assigned to the directly tin bonded aliphatic carbon atoms. The bonds of the sp$^{2}$-hybridized phenyl carbon atoms to the peripheral tin atoms cause an s orbital influence to the Sn–$C_{butyl}$ ($\delta = 10.69$ ppm) bond formation and thus an enlargement of the coupling constant $^{1}J(^{13}C^{117/119}Sn)$ from 295.91/309.81 to 377.38/394.82 Hz. The smaller coupling constant $^{1}J(^{13}C^{117/119}Sn)$ (295.91/309.81 Hz) of the signal at 8.32 ppm is significant for tetraalkyltin compounds and for that reason is assigned to the carbon atoms bonded to the central tin atom. The signals of the β and γ carbon atoms of the butyl chain lie very close together at $\delta = 31.66$ and 31.77 ppm. The presence of two non-equivalent tin centers at both ends of the butyl chain gives rise to couplings with two tin atoms, each coordinated by different organic ligands. Consequently, for each of these carbon atoms two coupling constants $^{2}J(^{13}C^{117/119}Sn)$ and $^{3}J(^{13}C^{117/119}Sn)$ were determined. Since aryl substituted organotin compounds cause larger $J(^{13}C,Sn)$ coupling constants then those of alkyl substituted compounds, the signal at $\delta = 31.77$ ppm with $^{3}J(^{13}C^{119}Sn) = 63.22$ Hz indicates a γ-position for the phenyl substituted peripheral tin atoms and allows an assignment of this signal to the carbon atom in γ-position to the phenyl substituted tin atom. The resonance at 31.36 ppm ($^{3}J(^{13}C^{119}Sn) = 57.77$ Hz) belongs to the remaining carbon atom. The resonances detected for **3** range from 8 to 140 ppm. The butyl carbon atoms bonded to the peripheral tin atoms are influenced particularly by the replacement of one phenyl group by chlorine in each dendron, which is reflected by a strong deshielded resonance at $\delta =$ 17.01 ppm. On the other hand, a reversed but smaller effect is observed for the β and γ carbon atoms of the butyl chain, which appear with a slight upfield shift at $\delta = 30.02$ and 30.98 ppm. The presence of the electron rich chlorine increases the s-character of the hybrid orbitals, participating in the Sn–C bond confirmed by an enlargement of the corresponding coupling constants $^{1}J(^{13}C^{117/119}Sn) = 405.99/424.52$ Hz by 28 Hz. The $^{13}C\text{-}\{^{1}H\}$ NMR spectra of **4** and **5** differ only slightly from that of **2**. The exchange of chlorine by hydrogen in **4** and by $C_5H_5$ in **5** causes an upfield shift of the signals of the butyl carbon atoms bonded to the peripheral tin atoms from $\delta = 17.01$ ppm in **3** to 10.24 ppm in **4** and 9.72 ppm in **5**. The $^{13}$C/Sn coupling constants diminish and show values close to those of **2**.

The $^{119}Sn\{^{1}H\}$ NMR spectra of **2** to **4** display for the two non-equivalent tin atoms two resonances with different intensities (Fig. 1). While the central tin atom is not much affected, the peripheral tin atoms display signals dependent upon the electronegativity of the different third ligand at tin at −136.65 ppm (**4**), −99.36 ppm (**2**) and +17.50 ppm (**3**).

The constitution of compounds **2**–**4**, has been certified also by MALDI-TOF mass spectrometric investigations. For all dendrimers the appropriate molecular ion could be detected as peak with the highest $m/z$ value (**2**: $m/z$ 1766.42 (Fig. 2), **3**: $m/z$ 1599.13 and **4**: $m/z$ 1462.39). The spectra indicate no signals assignable to impurities with imperfectly branched dendrimers or incomplete substitution reactions. The molecular ion peaks, which appear with the appropriate tin isotope ratios agreed very closely

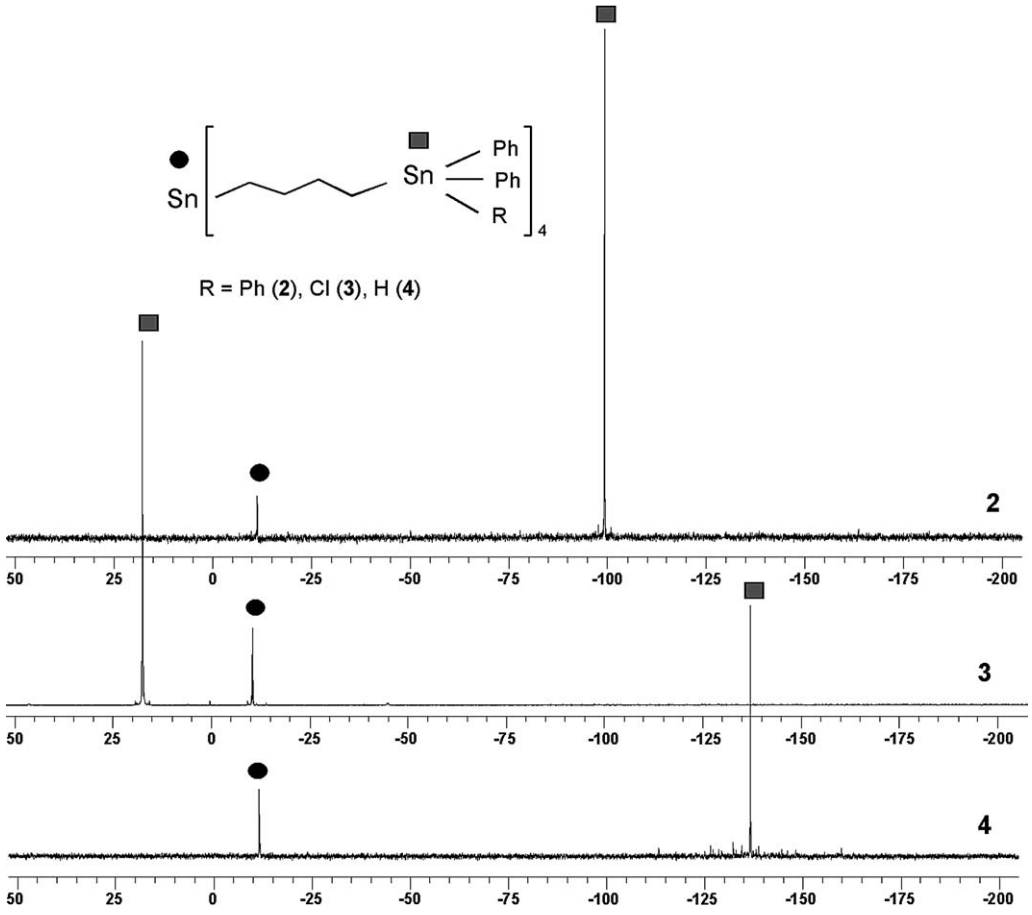



Fig. 1. $^{119}$Sn NMR spectra (149.21 MHz) of **2**, **3** in $CDCl_3$ and **4** in $C_6D_6$.

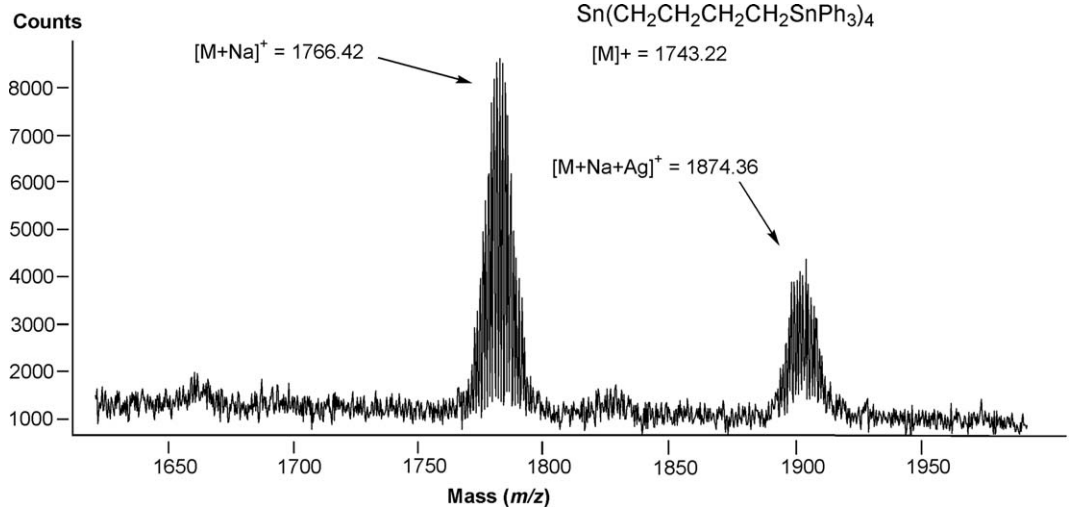
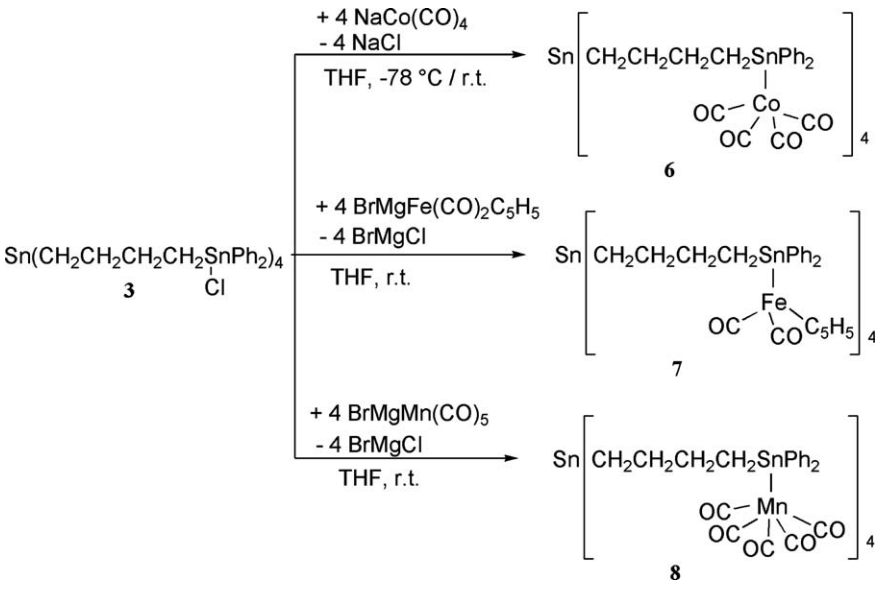



Fig. 2. MALDI-TOF mass spectrum of **2**.

with the calculated values. The MALDI-TOF mass spectrum of **3** exhibits a lower mass peak arising from the loss of two chlorine groups at $m/z$ 1530.33 $[M - 2Cl + Na]^+$. For all dendrimers no significant fragmentation could be observed.

### 2.3. Dendrimers with peripheral transition metal complexes

Dendrimer **3** containing four chlorine atoms bonded to the four peripheral tin atoms is a promising starting material for the synthesis of transition metal containing




Scheme 3.

dendrimers with a stable organotin core and four transition metals at the periphery potentially useful for homogeneous catalysis. To investigate this possibility, we treated **3** with a slight excess (4.1 equiv) of $NaCo(CO)_4$ in diethyl ether and $BrMgFe(CO)_2C_5H_5$, as well as $BrMgMn(CO)_5$ in THF. The new dendrimers $Sn[(CH_2)_4Sn\{Co(CO)_4\}Ph_2]_4$ (**6**), $Sn[(CH_2)_4Sn\{Fe(CO)_2C_5H_5\}Ph_2]_4$ (**7**), and $Sn[(CH_2)_4Sn\{Mn(CO)_5\}Ph_2]_4$ (**8**), respectively, are formed as a green viscous oil (**6**), as a brown viscous oil (**7**), and as a yellowish oil (**8**), respectively, and are isolated after repeated extraction with cold diethyl ether/pentane mixtures in satisfying yields (Scheme 3). They are soluble in aromatic hydrocarbons and THF, but insoluble in alkanes and diethyl ether. They are air sensitive and decompose on contact with atmospheric oxygen within a few hours accompanied by discoloration and solidification. On the other hand, **6**–**8** are stable on exposure to degassed water. This resistance allows removal of excess Grignard reagents by hydrolysis and isolation of the products in high purity.

The $^1H$ NMR spectra of **6**–**8** show strongly widened signals, presumably as a result of the broadening effect arising from the presence of transition metal containing ligands, whose interference prevent a determination of the hydrogen tin couplings. In contrast the resemblance to the spectra of the dendrimers **2**–**4**, and the good concordance of the relative intensities of the signals with the theoretical values makes a correct location possible. All $^1H$ NMR spectra exhibit the expected number of signals and could be analyzed without exception. For all transition metal derivatives the resonances for the $Sn^{\alpha}CH_2$ protons and the protons of the phenyl ligands were identified with almost identical chemical shift values as in the parent compound **2**. Differences were observed for the β, γ, and δ protons of the butenyl chains, which experience a slightly downfield shift caused by the presence of the new transition metal complex units.

The $^{13}C\{^1H\}$ NMR spectra of compounds **6**–**8** show just one signal for each carbon atom, demonstrating the purity of the derivatives and the consistence with the proposed structures. The replacement of the chlorine atoms at the surface of the dendrimer **2** by the fragments $Co(CO)_4$ in **6** and $Mn(CO)_5$ in **8** produced a diminution of the coupling constants, confirmed specifically by a strong downfield shift of the δ-carbon atom of the butenyl chain, whereas the remaining carbon atoms of this chain are less affected and maintain their original positions with only very light deviations. For **7** the Sn/C-coupling constants could not be observed. Even long-time measurements afforded no detection. The spectrum of **6** displays a slightly upfield shifted δ-carbon atom ($\delta = 17.94$ ppm) with a reduced coupling constant of $^1J(^{13}C^{117/119}Sn) = 320.16/335.15$ Hz. The introduction of $[Fe(CO)_2C_5H_5]$ units in **7** exerts similarly a large upfield shift of the δ-carbon atoms to $\delta = 15.41$ ppm. The $[Mn(CO)_5]$ ligands in **8** cause a further and stronger upfield shift to $\delta = 14.46$ ppm and a more intense reduction of the appropriate coupling constant $^1J(^{13}C^{117/119}Sn)$ (280.11/292.37 Hz). The characteristic carbonyl groups can be detected likewise in the expected region, as singlets at $\delta = 199.46$ ppm (**6**), 214.89 ppm (**7**), and 213.87 ppm (**8**).

The $^{119}Sn\{^1H\}$ NMR spectra of compounds **5**–**8** show only two signals each for the two different kinds of tin atoms and reflect the successful conversion of **3** and preclude the formation of uncompleted substitution products (Fig. 3).

Due to the drastic shifts of the appropriate $^{119}Sn\{^1H\}$ NMR resonances, the effect of the cyclopentadienyl groups and the transition metal ligands on the peripheral tin atoms can be pursued more simply and significantly than with the $^{13}C\{^1H\}$ NMR data. The extreme downfield location of the $^{119}Sn$ NMR signals is remarkable. While the cyclopentadienyl groups cause an upfield shift of the terminal tin atom resonances from $\delta = 17.50$ ppm for **3** to −70.65 ppm in **5**, the conversion of **3** to **6** and **7** accompanies simultaneous and

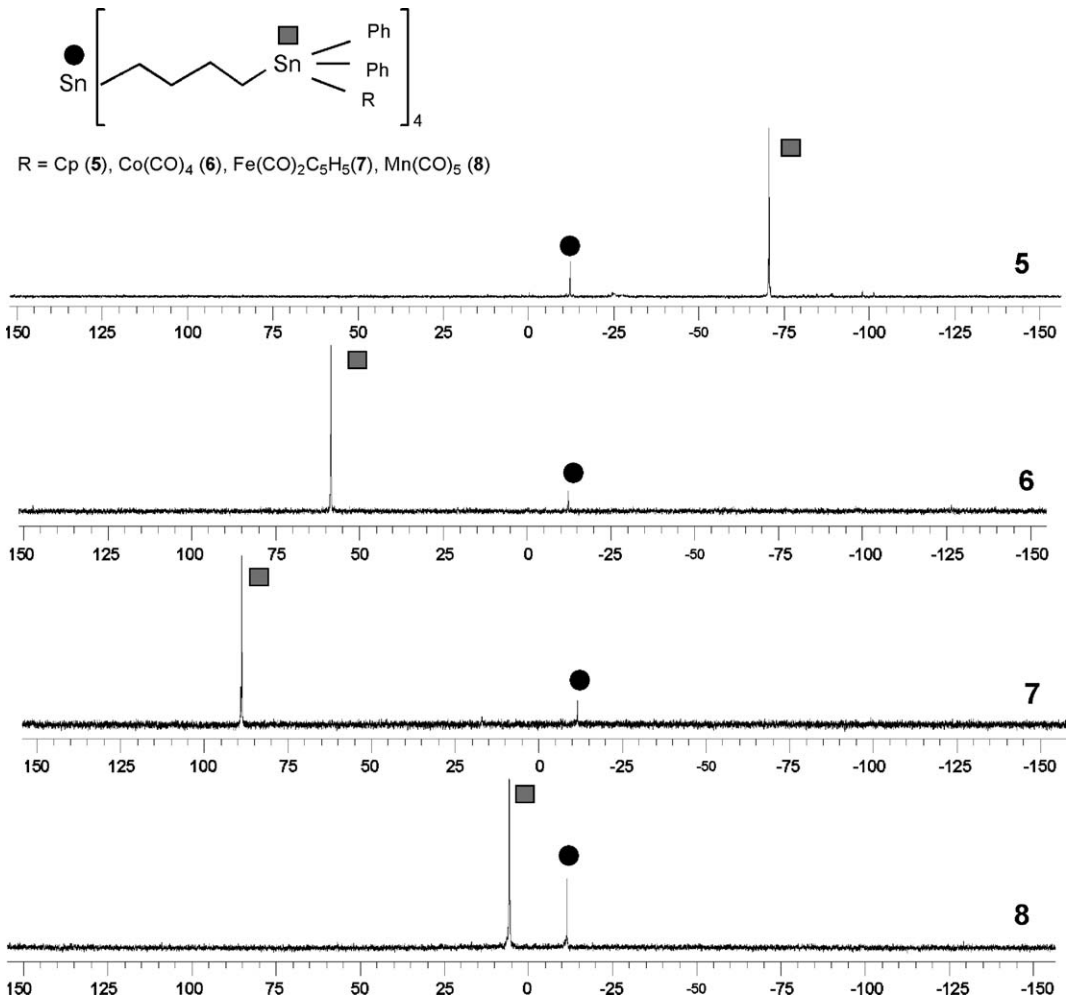



Fig. 3. $^{119}$Sn NMR spectra (149.21 MHz) of **5** and **6** in $C_6D_6$ and **7** and **8** in $CDCl_3$.

differentiated downfield shifts to 58.39 (**6**) and 88.65 ppm (**7**), respectively. In contrast **8** shows an upfield shifted resonance at $\delta = 5.61$ ppm for the same tin atoms. A correlation between these $^{119}$Sn NMR data and the magnitude of the corresponding $^{13}C^{117/119}Sn$ coupling constants is not producible. Obviously not only the electronic character of the peripheral tin atoms plays a role in these effects.

The IR spectra of **6**–**8** recorded in $CHCl_3$ show the predominant $\nu$(C=O) absorption bands in the typical regions of comparably modified organotin compounds [27].

Despite the application of different ionization methods, significant mass spectra could not be obtained for **5** and **6**. The thermolability and air sensibility of these compounds prevented a sufficient characterization by mass spectrometry. For dendrimers **7** and **8** the corresponding sodium ion adduct peaks $m/z$ 2165.39 $[M_7 + Na]^+$ and $m/z$ 2235.08 $[M_8 + Na]^+$ were detected satisfyingly with MALDI-TOF mass spectrometry.

## 3. Experimental

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 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 MHz) and ARX 400 ($^1$H, 400 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. Chemical shifts for $^{119}$Sn measurements are given relative to $(CH_3)_4Sn$. IR spectra were obtained on 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 reflection mode on an Applied Biosystems Voyager™-Elite mass spectrometer equipped with a nitrogen laser emitting at 337 nm. The acceleration voltage was set to 20 and 25 kV, respectively, with positive or negative ion-

ization. The mass spectrometer was externally calibrated with a mix of three peptides with different masses. Trans-indolacrylicacid (IAA) was used as MALDI matrix at a concentration 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 $CH_3CO_2Na$, KCl or AgI were used as ionization agents. Sonification was applied to speed up mixing. One microlitre 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. $CH_2$=CH-$CH_2CH_2Br$, anhydrous HCl(g), $LiAlH_4$, $SnCl_4$, $Ph_3SnCl$, $Sn(CH{=}CH_2)_4$, $Sn(CH_2CH{=}CH_2)_4$, $Mn_2(CO)_{10}$, and $[Fe(CO)_2\text{-}\eta^5\text{-}C_5H_5]_2$ were used as purchased. $Ph_3SnH$ [28], $NaC_5H_5$ [25], $Na[Co(CO)_4]$ [29], $BrMg[Fe(CO)_2\text{-}\eta^5\text{-}C_5H_5]$ [30], and $BrMg[Mn(CO)_5]$ [30] were prepared according to published procedures.

### 3.1. Hydrostannation of tetravinylstannane

Freshly distilled $Ph_3SnH$ (11 g, 31.5 mmol) and AIBN (5 mol%, 0.3 g, 1.5 mmol) were placed in a 50 ml flask and stirred for 0.5 h at room temperature. Then $Sn(CH{=}CH_2)_4$ (1.43 g, 6.3 mmol) was added slowly within 0.5 h. After stirring the reaction mixture overnight at ambient temperature, pentane was added to the viscous crude product to precipitate a solid. Filtration, subsequent washing of the residue three times with a mixture of $Et_2O$/pentane (50:50) and removal of the solvents in vacuum ($10^{-2}$ mbar) yielded $(Ph_3SnCH_2)_2$ as a light yellow solid.

Yield: 1.97 g (2.7 mmol), m.p. 204–205 °C (Lit.: 205–207 °C [19]). $^1$H NMR (200.13 MHz, $CDCl_3$): $\delta$ 1.94 (m, 4H, C$H_2$SnPh$_3$), 7.33–8.03 (m, 12H, Ph–H$_o$), 7.57–7.81 (m, 18H, Ph–H$_{m/p}$). $^{13}$C{$^1$H} NMR (50.32 MHz, $CDCl_3$): $\delta$ 8.20 [$^1J(^{13}C^{117/119}Sn)$ = 297.32/311.10 Hz, $CH_2SnPh_3$], 128.97 [$^3J(^{13}C^{117/119}Sn)$ = 136.37/142.64 Hz, Ph–C$_m$], 129.34 [$^4J(^{13}C^{117/119}Sn)$ = 10.97/11.48 Hz, Ph–C$_p$], 137.25 [$^1J(^{13}C^{117/119}Sn)$ = 456.75/477.76 Hz, Ph–C$_{ipso}$], 137.70 [$^2J(^{13}C^{117/119}Sn)$ = 44.62/46.67 Hz, Ph–C$_o$]. MS (192 °C): $m/z$ (%): 728.6 (0.02) $[M]^+$, 659 (2) $[M - C_2H_4]^+$, 582 (1) $[M - C_2H_4 - C_6H_5]^+$, 505 (3) $[M - C_2H_4 - 2C_6H_5]^+$, 352 (99) $[M - C_2H_4 - Sn(C_6H_5)_3]^+$, 120 (24) $[Sn]^+$. Anal. Calc. for $C_{38}H_{34}Sn_2$ (728.07 g/mol): C, 62.69; H, 4.71. Found: C, 62.39; H, 4.39%.

### 3.2. Hydrostannation of tetraallylstannane

In analogy with the hydrostannation of $Sn(CH{=}CH_2)_4$, $Sn(CH_2CH{=}CH_2)_4$ (1.37 g, 4.84 mmol) was added slowly at room temperature to a mixture of $Ph_3SnH$ (8.5 g, 24.2 mmol) and AIBN (5 mol%, 0.2 g, 1.2 mmol). After the reaction and workup $(Ph_3SnCH_2)_2CH_2$ [21] was obtained as a yellow powder.

Yield: 0.47 g (1.7 mmol). $^1$H NMR (200.13 MHz, $CDCl_3$): $\delta$ 1.39 (m, 4H, C$H_2$SnPh$_3$), 1.49–1.80 (m, 2H, C$H_2$CH$_2$SnPh$_3$), 7.23–8.11 (m, 12H, Ph–H$_o$), 7.65–7.93 (m, 18H, Ph–H$_{m/p}$). $^{13}$C{$^1$H} NMR (50.32 MHz, $CDCl_3$): $\delta$ 8.17 [$^1J(^{13}C^{117/119}Sn)$ = 296.22/309.83 Hz, $CH_2CH_2SnPh_3$], 30.20 [$^2J(^{13}CSn)$ = 43.31/45.30 Hz, $CH_2CH_2SnPh_3$], 128.77 [$^3J(^{13}C^{117/119}Sn)$ = 137.73/140.07 Hz, Ph–C$_m$], 129.15 [$^4J(^{13}C^{117/119}Sn)$ = 11.1/11.64 Hz, Ph–C$_p$], 137.54 [$^1J(^{13}C^{117/119}Sn)$ = 455.53/476.48 Hz, Ph–C$_{ipso}$], 137.87 [$^2J(^{13}C^{117/119}Sn)$ = 45.51/47.60 Hz, Ph–C$_o$]. MS (203 °C): $m/z$ (%): 743 (0.03) $[M]^+$, 701 (1) $[M - C_3H_6]^+$, 624 (3) $[M - C_3H_6 - C_6H_5]^+$, 547 (1) $[M - C_3H_6 - 2C_6H_5]^+$, 352 (99) $[M - C_3H_6 - Sn(C_6H_5)_3]^+$, 120 (24) $[Sn]^+$. Anal. Calc. for $C_{39}H_{36}Sn_2$ (742.09 g/mol): C, 63.12; H, 4.89. Found: C, 63.09; H, 5.27%.

### 3.3. Synthesis of $Sn(CH_2CH_2CH{=}CH_2)_4$ (1)

A solution of $CH_2{=}CHCH_2CH_2MgBr$ in THF (100 ml), prepared from $CH_2{=}CHCH_2CH_2Br$ (20 g, 148 mmol) with excess magnesium turnings (4.0 g, 165 mmol) was placed in a 250 ml flask and cooled to 0 °C, before freshly distilled $SnCl_4$ (9.6 g, 37 mmol) was added cautiously within 1 h. The solution was stirred for 0.5 h at 0 °C and subsequently for 5 h at ambient temperature. After cooling to 0 °C, the reaction mixture was hydrolyzed slowly with water. The organic fraction was extracted with $Et_2O$, washed several times with saturated $NH_4Cl$ solution and dried over $Na_2SO_4$. After the removal of all volatiles, **1** was obtained as a light yellow oil.

Yield 9.50 g (76%), b.p. 60–64 °C/0.06 mbar (Lit. 78–82 °C/0.04 mmHg [22]). IR (KBr/film): $\nu$(C=C) 1639 cm$^{-1}$(s). $^1$H NMR (200.13 MHz, $CDCl_3$): $\delta$ 0.96 [m, $^2J(^1H^{117/119}Sn)$ = 46.85/48.79 Hz, 8H, $SnCH_2$], 2.29 (m, 8H, $SnCH_2CH_2$), 4.97 (m, 8H, $=CH_2$), 5.90 (m, 4H, CH). $^{13}$C{$^1$H} NMR (50.32 MHz, $CDCl_3$): $\delta$ 8.46 [$^1J(^{13}C^{117/119}Sn)$ = 300.27/314.17 Hz, $SnCH_2$], 30.78 [$^2J(^{13}C^{119}Sn)$ = 17.98 Hz, $SnCH_2C$], 112.99 ($=CH_2$), 141.79 [$^3J(^{13}CSn)$ = 50.14 Hz, CH]. $^{119}$Sn{$^1$H} NMR (149.21 MHz, $CDCl_3$): $\delta$ −5.6. MS (110 °C): $m/z$ (%): 285 (8) $[M - C_4H_7]^+$, 230 (7) $[M - 2C_4H_7]^+$, 175 (11) $[M - 3C_4H_7]^+$, 120 (6) $[Sn]^+$. Anal. Calc. for $C_{16}H_{28}Sn$ (339.1 g/mol): C, 56.67; H, 8.32. Found: C, 56.59; H, 8.29%.

### 3.4. Synthesis of $Sn[CH_2CH_2CH_2CH_2Sn(C_6H_5)_3]_4$ (2)

Freshly distilled $Ph_3SnH$ (22.1 g, 63 mmol) was treated with AIBN (0.50 g, 5 mol%, 3 mmol) and stirred at room temperature for 0.5 h. Then **1** (5.33 g, 15.7 mmol) was added slowly within 0.5 h. Stirring of the mixture was continued for 12 h at ambient temperature, during which the reaction solution solidified. The resulting viscous mixture was dissolved in 10 ml of toluene and stirred for additional 12 h. Addition of pentane (25 ml) to the light yellow solution resulted in the formation of a white precipitate. The yellow supernatant was filtered off and the product was washed several times with a mixture of pentane/$Et_2O$ (50:50, 25 ml). Removal of the solvents in a vacuum ($10^{-2}$ mbar) remained white solid **2**.

Yield: 25.7 g (94%), m.p. 109 °C. $^1$H NMR (200.13 MHz, $CDCl_3$): $\delta$ 0.45–0.80 (m, 8H, $SnCH_2$), 1.32–1.58 (m, 16H, $SnCH_2CH_2$ and $SnCH_2CH_2CH_2$), 1.58–1.76 (m, 8H, $Ph_3SnCH_2$), 7.30–7.42 (m, 36H, Ph–$H_{m/p}$), 7.51–7.62 (m, 24H, Ph–$H_o$). $^{13}$C{$^1$H} NMR (50.32 MHz, $CDCl_3$): $\delta$ 8.32 [$^1J(^{13}C^{117/119}Sn) = 295.91/309.81$ Hz, $SnCH_2$], 10.69 [$^1J(^{13}C^{117/119}Sn) = 377.38/394.82$ Hz, $Ph_3SnCH_2$], 31.36 [$^3J(^{13}CSn) = 57.77$ Hz, $^2J(^{13}CSn) = 22.07$ Hz, $SnCH_2CH_2C$], 31.77 [$^2J(^{13}CSn) = 18.23$ Hz, $^3J(^{13}CSn) = 63.22$ Hz, $SnCH_2C$], 128.42 [$^2J(^{13}CSn) = 46.87$ Hz, Ph–$C_m$], 128.76 [$^4J(^{13}CSn) = 12.26$ Hz, Ph–$C_p$], 137.01 [$^3J(^{13}CSn) = 35.42$ Hz, Ph–$C_o$], 139.11 [$^1J(^{13}C^{117/119}Sn) = 458.58/479.83$ Hz, Ph–$C_{ipso}$]. $^{119}$Sn{$^1$H} NMR (149.21 MHz, $CDCl_3$): $\delta$ −11.45 ($SnC_4$), −99.36 ($SnPh_3$). MS-MALDI-TOF (IAA, thf): *m/z* (calc.) 1766.42 (1766.22) $[M + Na]^+$, 1874.36 (1874.09) $[M + Na + Ag]^+$. Anal. Calc. for $C_{88}H_{92}Sn_5$ (1743.15 g/mol): C, 60.64; H, 5.32. Found: C, 60.42; H, 5.30%.

### 3.5. Synthesis of $Sn[CH_2CH_2CH_2CH_2SnCl(C_6H_5)_2]_4$ (3)

A 50 ml flask equipped with an additional funnel containing a colorless solution of **2** (10.5 g, 6 mmol) in 30 ml of $CH_2Cl_2$ was cooled to −78 °C. The additional funnel was charged with a 4 M solution of anhydrous HCl(g) in $Et_2O$ (6 ml, 24 mmol), which was added dropwise to the vigorously stirred solution of **2** within 0.5 h. After 5 h at −78 °C, the reaction mixture was gradually warmed to room temperature and stirred for additional 12 h. The resulting benzene and the solvents were evacuated under vacuum ($10^{-2}$ mbar). **3** was obtained as a light yellow viscous oil.

Yield: 8.67 g (92%). $^1$H NMR (200.13 MHz, $CDCl_3$): $\delta$ 0.80–1.02 (m, 8H, $SnCH_2$), 1.60–1.80 (m, 8H, $Ph_2SnCH_2$), 1.82–2.06 (m, 16H, $SnCH_2CH_2$ and $SnCH_2CH_2CH_2$), 7.47–7.68 (m, 36H, Ph–$H_{m/p}$), 7.71–7.88 (m, 24H, Ph–$H_o$). $^{13}$C{$^1$H} NMR (50.32 MHz, $CDCl_3$): $\delta$ 8.32 [$^1J(^{13}C^{117/119}Sn) = 295.91/309.81$ Hz, $SnCH_2$], 17.01 [$^1J(^{13}C^{117/119}Sn) = 405.99/424.52$ Hz, $Ph_2SnCH_2$], 30.02 [$^2J(^{13}CSn) = 27.79$ Hz, $^3J(^{13}CSn) = 58.04$ Hz, $SnCH_2CH_2C$], 30.98 [$^3J(^{13}CSn) = 69.210$ Hz, $^2J(^{13}CSn) = 19.35$ Hz, $SnCH_2C$], 128.84 [$^2J(^{13}C^{117/119}Sn) = 46.32/47.96$ Hz, Ph–$C_o$], 130.00 [$^4J(^{13}CSn) = 12.53$ Hz, Ph–$C_p$], 135.64 [$^3J(^{13}C^{117/119}Sn) = 56.68/58.86$ Hz, Ph–$C_m$], 138.89 [$^1J(^{13}C^{117/119}Sn) = 512.80/536.78$ Hz, Ph–$C_{ipso}$]. $^{119}$Sn{$^1$H} NMR (149.21 MHz, $CDCl_3$): $\delta$ −10.46 ($SnC_4$), 17.50 ($SnPh_2$). MS-MALDI-TOF (IAA, thf): *m/z* (calc.) 1576.95 (1576.62) $[M]^+$, 1599.13 (1599.62) $[M + Na]^+$, 1638.93 (1638.62) $[M + Na + K]^+$, 1530.33 $[M - 2Cl + Na]^+$. Anal. Calc. for $C_{64}H_{72}Cl_4Sn_5$ (1576.54 g/mol): C, 48.76; H, 4.60. Found: C, 48.42; H, 4.30%.

### 3.6. Synthesis of $Sn[CH_2CH_2CH_2CH_2SnH(C_6H_5)_2]_4$ (4)

$LiAlH_4$ (0.19 g, 5 mmol) was placed in a 250 ml three-necked flask equipped with reflux condenser and addition funnel and dissolved in 100 ml of $Et_2O$ to give a dark grey suspension. A solution of **3** (7.9 g, 5 mmol) in 100 ml of $Et_2O$ was syringed into the addition funnel and added dropwise at 0 °C within 1 h. The resulting brown solution was stirred for 1 h at this temperature and 5 h at room temperature, before it was hydrolyzed carefully with water (0.1 g, 5.5 mmol) in 20 ml of dioxane at 0 °C. After stirring for 0.5 h at room temperature, the reaction mixture was filtered and extracted three times with $Et_2O$ (25 ml). The combined organic fractions were washed twice with a saturated solution of $NH_4Cl$ (20 ml) and twice with a saturated solution of NaCl (20 ml) in water. After drying with $Na_2SO_4$ and evaporation of the solvents in vacuum ($10^{-2}$ mbar), **4** was isolated as a colorless viscous oil.

Yield: 6.69 g (93%). IR (KBr/Film): $\nu$(Sn–H) 1829 cm$^{-1}$ (s). $^1$H NMR (200.13 MHz, $C_6D_6$): $\delta$ 0.57–0.98 (m, 8H, $SnCH_2$), 1.04–1.40 (m, 8H, $Ph_2SnCH_2$), 1.41–1.80 (m, 16H, $SnCH_2CH_2$ and $SnCH_2CH_2CH_2$), 6.37 [s, $^1J(^1H^{117/119}Sn) = 1723.17/1803.76$ Hz, 4H, SnH], 7.05–7.28 (m, 36H, Ph–$H_{m/p}$), 7.35–7.71 (m, 24H, Ph–$H_o$). $^{13}$C{$^1$H} NMR (50.32 MHz, $C_6D_6$): $\delta$ 8.82 [$^1J(^{13}C^{117/119}Sn) = 295.64/309.26$ Hz, $SnCH_2$], 10.24 [$^1J(^{13}C^{117/119}Sn) = 376.57/394.56$ Hz, $Ph_2SnCH_2$], 31.84 [$^3J(^{13}CSn) = 59.67$ Hz, $^2J(^{13}CSn) = 19.35$ Hz, $SnCH_2CH_2$], 32.17 [$^2J(^{13}CSn) = 22.62$ Hz, $^3J(^{13}CSn) = 52.861$ Hz, $SnCH_2CH_2CH_2$], 128.83 [$^4J(^{13}CSn) = 10.89$ Hz, Ph–$C_p$], 129.05 [$^2J(^{13}C^{117/119}Sn) = 47.68$ Hz, Ph–$C_m$], 137.51 [$^3J(^{13}C^{117/119}Sn) = 36.24$ Hz, Ph–$C_o$], 138.30 [$^1J(^{13}C^{117/119}Sn) = 465.67/487.46$ Hz, Ph–$C_{ipso}$]. $^{119}$Sn{$^1$H} NMR (149.21 MHz, $C_6D_6$,): $\delta$ −11.58 ($SnC_4$), −136.65 ($SnPh_2$). MS-MALDI-TOF (IAA, thf): *m/z* (calc.): 1462.39 (1461.84) $[M + Na]^+$. Anal. Calc. for $C_{64}H_{76}Sn_5$ (1438.76 g/mol): C, 53.43; H, 5.32. Found: C, 53.14; H, 5.11%.

### 3.7. Synthesis of $Sn[CH_2CH_2CH_2CH_2Sn(C_5H_5)(C_6H_5)_2]_4$ (5)

A solution of **3** (4.0 g, 2.54 mmol) in toluene (25 ml) was placed in a 50 ml flask equipped with an addition funnel, and cooled to 0 °C. A suspension of $NaC_5H_5$ (1.35 g, 15.30 mmol) in toluene (25 ml) was syringed into the addition funnel, and added slowly to the solution. The light yellow solution was stirred for 48 h at room temperature. After cooling to 0 °C the reaction mixture was filtered and the clear yellow solution concentrated under vacuum ($10^{-2}$ mbar). The product was further purified by repeated extraction with cold toluene. After removal of the solvents in vacuum ($10^{-2}$ mbar) **5** was obtained as a viscous yellow oil.

Yield: 3.05 g (71%). $^1$H NMR (200.13 MHz, $C_6D_6$,): $\delta$ 0.48–0.81 (m, 8H, $SnCH_2$), 0.85–1.15 (m, 8H, $Ph_2SnCH_2$), 1.22–1.67 (m, 16H, $SnCH_2CH_2$ and $SnCH_2CH_2CH_2$), 6.28 (s, $^2J(^1HSn) = 22.60/23.64$ Hz, 20H, Cp-H), 7.05–7.30 (m, 36H, Ph–$H_{m/p}$), 7.37–7.68 (m, 24H, Ph–$H_o$). $^{13}$C{$^1$H} NMR (50.32 MHz, $C_6D_6$): $\delta$ 8.75 [$^1J(^{13}C^{117/119}Sn) = 284.46/297.55$ Hz, $SnCH_2$], 9.72 [$^1J(^{13}C^{117/119}Sn) = 385.28/405.72$ Hz, $Ph_2SnCH_2$], 31.74 [$^2J(^{13}CSn) = 27.80$ Hz, $^3J(^{13}CSn) = 56.13$ Hz, $SnCH_2CH_2CH_2$], 32.06 [$^3J(^{13}CSn) = 68.12$ Hz, $^2J(^{13}CSn) = 19.35$ Hz, $SnCH_2CH_2$],

113.64 (Cp-C), 128.48 [$^3J(^{13}C^{117/119}Sn) = 52.86$ Hz, Ph–$C_m$], 129.32 [$^4J(^{13}CSn) = 10.90$ Hz, Ph–$C_p$], 136.84 [$^2J(^{13}CSn) = 35.42$ Hz, Ph–$C_o$], 140.21 [$^1J(^{13}C^{117/119}Sn) =$ 438.96/459.40 Hz, Ph–$C_{ipso}$]. $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $C_6D_6$,): $\delta$ −12.36 ($SnC_4$), −70.65 ($SnPh_2$). MS-MALDI-TOF (IAA, thf): *m/z*: no signal. Anal. Calc. for $C_{84}H_{92}Sn_5$ (1695.10 g/mol): C, 59.52; H, 5.47. Found: C, 59.01; H, 5.13%.

### 3.8. Synthesis of $Sn\{CH_2CH_2CH_2CH_2Sn[Co(CO)_4](C_6H_5)_2\}_4$ (6)

$NaCo(CO)_4$ (2.72 g, 14 mmol) dissolved in THF (20 ml) was put into a 50 ml flask with an addition funnel and cooled to −78 °C. A solution of **3** (5.4 g, 3.4 mmol) in 20 ml of THF was added dropwise under vigorous stirring. The clear light brown reaction mixture was stirred 3 h at this temperature and overnight at room temperature. The precipitated NaCl was removed by filtration and volatiles were evaporated in vacuum ($10^{-2}$ mbar). Repeated dissolving of the remaining crude product in toluene and precipitating it again with cold $CH_3OH$ gave **6** as a viscous green oil.

Yield: 5.83 g (81%). IR (KBr/film): $\nu$(C≡O) 2084 (s), 2020 (s), 2002 $cm^{-1}$(s). $^1H$ NMR (200.13 MHz, $C_6D_6$): $\delta$ 0.48–0.90 (m, 8H, $SnCH_2$), 1.43–1.65 (m, 8H, $Ph_2SnCH_2$), 1.63–1.99 (m, 16H, $SnCH_2CH_2$ and $SnCH_2CH_2CH_2$), 6.97–7.34 (m, 36H, Ph–$H_{m/p}$), 7.39–7.87 (m, 24H, Ph–$H_o$). $^{13}C\{^1H\}$ NMR (50.32 MHz, $C_6D_6$,): $\delta$ 8.55 [$^1J$ ($^{13}C^{117/119}Sn$) = 295.34/308.99 Hz, $SnCH_2$], 17.94 [$^1J$ ($^{13}C^{117/119}Sn$) = 320.16/335.15 Hz, $Ph_2SnCH_2$], 31.78 [$^3J(^{13}CSn) = 73.30$ Hz, $^2J(^{13}CSn) = 18.26$ Hz, $SnCH_2CH_2$], 32.19 [$^2J$ ($^{13}CSn$) = 25.07 Hz, $^3J(^{13}CSn) = 56.95$ Hz, $SnCH_2CH_2CH_2$], 129.10 [$^2J(^{13}C^{117/119}Sn) = 58.86$ Hz, Ph–$C_m$], 129.57 [$^4J(^{13}CSn) = 11.44$ Hz, Ph–$C_p$], 136.30 [$^3J(^{13}C^{117/119}Sn) =$ 39.51 Hz, Ph–$C_o$], 141.26 [$^1J(^{13}C^{117/119}Sn) = 394.23/412.53$ Hz, Ph–$C_{ipso}$], 199.46 (CO). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $C_6D_6$,): $\delta$ −12.35 (Sn), 58.39 ($SnPh_2$). MS-MALDI-TOF (IAA, thf): *m/z* no signal. Anal. Calc. for $C_{80}H_{72}O_{16}Co_4Sn_5$ (2118.62 g/mol): C, 45.35; H, 3.43. Found: C, 44.92; H, 3.45%.

### 3.9. Synthesis of $Sn\{CH_2CH_2CH_2CH_2Sn[Fe(CO)_2)(C_5H_5)](C_6H_5)_2\}_4$ (7)

A solution of **3** (0.8 g, 0.51 mmol) in THF (25 ml) was dropped slowly within 1 h at room temperature to a dark red solution of $BrMgFe(CO)_2(C_5H_5)$, prepared from $[Fe(CO)_2C_5H_5]_2$ (0.39 g, 1.1 mmol), $BrCH_2CH_2Br$ (0.19 g, 1.1 mmol), and Mg turnings (0.12 g, 5 mmol) in 50 ml of THF. After 5 h stirring at ambient temperature the reaction mixture was cooled to 0 °C, hydrolyzed carefully with degassed and nitrogen saturated water, then extracted three times with $Et_2O$ (25 ml). The combined organic fractions were washed with a saturated solution of $NH_4Cl$ in degassed water (50 ml), three times with a saturated solution of NaCl (50 ml) in degassed water, and dried over $Na_2SO_4$. The solvents were removed at reduced pressure ($10^{-2}$ mbar). Further purification of the product was achieved by dissolving the residue several times in $CH_2Cl_2$ and precipitating it by adding $Et_2O$/pentane (50:50). Evaporation of volatiles and drying in a vacuum ($10^{-2}$ mbar) gave **7** as viscous brown oil.

Yield: 0.96 g (88%). IR (KBr/film): $\nu$(C≡O) 1932 (s), 1985 $cm^{-1}$(s). $^1H$ NMR (400.13 MHz, $CDCl_3$): $\delta$ 0.56–0.84 (m, 8H, $SnCH_2$), 1.12–1.78 (m, 16H, $SnCH_2CH_2$ and $SnCH_2CH_2CH_2$), 1.82–2.09 (m, 8H, $Ph_2SnCH_2$), 4.40–5.10 (m, 20H, Cp-H), 6.98–7.51 (m, 36H, Ph–$H_{m/p}$), 7.51–7.90 (m, 24H, Ph–$H_o$). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$,): $\delta$ 8.23 ($SnCH_2$), 15.41 ($Ph_2SnCH_2$), 31.74 ($SnCH_2CH_2$), 32.23 ($SnCH_2CH_2CH_2$), 81.95 (Cp–C), 127.81 (Ph–$C_p$), 128.01 (Ph–$C_m$), 136.33 (Ph–$C_o$), 144.77 (Ph–$C_{ipso}$), 214.89 (CO). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$,): $\delta$ −11.68 (Sn), 88.65 ($Ph_2Sn$). MS-MALDI-TOF (ACCA, thf): *m/z* (calc.): 2165.39 (2165.64) $[M + Na]^+$, 2271.54 (2273.51) $[M + Na + Ag]^+$, 2056.20 $[M - CO]^+$. Anal. Calc. for $C_{92}H_{92}O_8Fe_4Sn_5$ (2142.58 g/mol): C, 51.57; H, 4.33. Found: C, 51.09; H, 4.17%.

### 3.10. Synthesis of $Sn\{CH_2CH_2CH_2CH_2Sn[Mn(CO)_5](C_6H_5)_2\}_4$ (8)

In analogy to **7**, a solution of **3** (0.8 g, 0.5 mmol) in 25 ml of THF was reacted at room temperature with a dark red solution of $BrMgMn(CO)_5$, prepared from $[Mn(CO)_5]_2$ (0.43 g, 1.1 mmol), $BrCH_2CH_2Br$ (0.20 g, 1.1 mmol), and Mg (0.12 g, 5 mmol) in 50 ml of THF. After stirring for 5 h at room temperature and workup, **8** was obtained as a viscous orange oil.

Yield: 0.87 g (79%). IR (KBr/film): $\nu$(C≡O) 1987 (s), 2005 (s), 2090 $cm^{-1}$(s). $^1H$ NMR (200.13 MHz, $CDCl_3$,): $\delta$ 0.33–0.91 (m, 8H, $SnCH_2$), 1.33–1.50 (m, 8H, $Ph_2SnCH_2$), 1.51–1.70 (m, 16H, $SnCH_2CH_2$ and $SnCH_2CH_2CH_2$), 7.26–7.52 (m, 36H, Ph–$H_{m/p}$), 7.54–7.81 (m, 24H, Ph–$H_o$). $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): $\delta$ 8.20 [$^1J(^{13}C^{117/119}Sn) = 295.64/308.99$ Hz, $SnC_4$], 14.46 [$^1J(^{13}C^{117/119}Sn) = 280.11/292.37$ Hz, $Ph_2SnCH_2$], 31.78 [$^3J(^{13}CSn) = 73.30$ Hz, $^2J(^{13}CSn) = 18.26$ Hz, $SnCH_2CH_2$], 32.19 [$^2J(^{13}CSn) = 25.07$ Hz, $^3J(^{13}CSn) = 56.95$ Hz, $SnCH_2CH_2CH_2$], 128.28 [$^4J(^{13}CSn) = 11.99$ Hz, Ph–$C_p$], 128.29 [$^2J(^{13}C^{117/119}Sn) = 43.87$ Hz, Ph–$C_m$], 136.36 [$^3J(^{13}C^{117/119}Sn) = 34.84$ Hz, Ph–$C_o$], 141.49 [$^1J(^{13}C^{117/119}Sn)$ = 334.06/350.14 Hz, Ph–$C_{ipso}$], 213.87 (CO). $^{119}Sn\{^1H\}$ NMR (149.21 MHz, $CDCl_3$,): $\delta$ −11.54 (Sn); 5.61 ($Ph_2Sn$). MS-MALDI-TOF (IAA, thf): *m/z* (calc.): 2235.08 (2237.76) $[M + Na]^+$, 2257.73 (2260.76) $[M + 2Na]^+$. Anal. Calc. for $C_{84}H_{72}O_{20}Mn_4Sn_5$ (2214.69 g/mol): C, 45.56; H, 3.28. Found: C, 45.44; H, 3.30%.

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