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Tetrakis(trimethylstannyl) and bis(trimethylstannyl)dimethyl Group 14 element compounds, determination of coupling signs and measurements of isotope induced chemical shifts $^1\Delta^{12/13}C(^{119}Sn)$

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Abstract

Tetrakis(trimethylstannyl) Group 14 element compounds, $(Me_3Sn)_4M$ [M = C (**1**), Si (**2**), Ge (**3**), Sn (**4**)] and bis(trimethylstannyl)dimethyl Group 14 element compounds (**1a**–**3a**) were prepared and studied by ^1H-, ^{13}C-, ^{29}Si-, ^{73}Ge-, and ^{119}Sn-NMR spectroscopy. The signs of $^1J(^{117/119}Sn,M)$ were determined [M = ^{13}C, ^{29}Si, ^{73}Ge, ^{119}Sn; all reduced coupling constants $^1K(Sn,M) > 0$]. In the series **1**–**4**, the geminal coupling constants $^2J(Sn,M,Sn)$ are negative for M = C, Si, Ge, whereas the coupling sign is positive for M = Sn in **4**. In the cases of **1a**–**4a**, this geminal coupling constant is always positive. In the same series the reduced coupling constants $^2K(Sn,M,^{13}C)$ are positive for **2a**–**4a** but negative for **1a**. All reduced coupling constants $^3K(Sn,M,Sn,^{13}C)$ are positive. Isotope induced chemical shifts $^1\Delta^{12/13}C(^{119}Sn)$ cover a fairly large range of ca. 15 ppb. The relationship of this parameter with the magnitude of $^1J(^{119}Sn,^{13}C)$ is not straightforward, and there is also no clear influence of the group electronegativity of substituents. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Germanium; Silicon; Tin; Coupling constants; Sign determination

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1. Introduction

Our understanding of NMR parameters of organometallic compounds depends greatly on data of complete series of related derivatives [1]. In this respect, compounds of Group 14 elements are particularly attractive since numerous homologous derivatives of carbon, silicon, germanium and tin are readily accessible and all can be studied by NMR, taking advantage of the presence of the spin-1/2 nuclei ^{13}C, ^{29}Si, $^{117/119}Sn$ and the quadrupolar nucleus ^{73}Ge ($I = 9/2$). Unfortunately, considering the highly NMR-sensitive spin-1/2 nucleus ^{207}Pb, comparable lead compounds are not always available. However, recent NMR studies on organolead compounds [2] have demonstrated a special role of the ^{207}Pb nucleus. This can most likely be traced to relativistic effects which are of great importance only for NMR parameters of the most heavy nuclei [3]. The present work focuses on two series of compounds **1**–**4** and **1a**–**4a** with emphasis on the determination of signs of various coupling constants (only a few absolute signs have been determined for these compounds as yet), and on the measurements of isotope induced chemical shifts $^1\Delta^{12/13}C(^{119}Sn)$. The knowledge of the coupling signs is essential if one aims for a meaningful discussion of the magnitude of coupling constants. Isotope induced chemical shifts $^1\Delta^{12/13}C(^{119}Sn)$ for organotin compounds [4–6] have received scant attention so far, although these data can be readily obtained and should reveal information on changes in the nature of the Sn–C bond.

$(Me_3Sn)_4M$	$(Me_3Sn)_2MMe_2$
1 2 3 4	**1a 2a 3a 4a**
M = C, Si, Ge, Sn	M = C, Si, Ge, Sn

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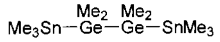
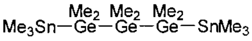
2. Results and discussion

2.1. Synthesis

The synthesis of all compounds studied involved the preparation of Me_3SnLi in THF and its reaction with the respective element halides (except in the case of **4**). The preparation of **1** [7], **2** [8], **3** [9], **1a** [10] and **2a** [11] was achieved by following the literature procedures. The synthesis of compound **4** was attempted at first by preparing a solution of $(Me_3Sn)_3SnLi$ from Me_3SnLi and $Me_3SnSnMe_3$ [12] and reacting it with Me_3SnCl. However, his method did not work in our hands. Then we attempted to reproduce the results [13] when only Me_3SnLi in THF was used and $(Me_3Sn)_3SnLi$ was formed in situ after removal of THF. The description of this procedure turned out to be inaccurate, and we failed in several attempts to obtain defined products after addition of Me_3SnCl. Only after some modifications, did it prove possible to obtain **4** in low yield. Compound **3a** has not been reported before. It was synthesized in the same way as described for compound **2a** [11]. However, this synthesis led to side products (not observed in the reaction with Me_2SiCl_2), of which **3b** and **3c** were identified by their NMR spectra. Mass spectra indicate that there are also chains with at least four Me_2Ge units present. However, these derivatives were not detected in the NMR spectra. It was not possible to separate **3a** completely from **3b** and **3c** by distillation. Apparently, similar side reactions dominate in the 2:1 reaction of Me_3SnLi in THF with Me_2SnCl_2; instead of **4a** a complex mixture of methyltin compounds was formed, of which the components have not been identified as yet.


$Me_3Sn{-}\overset{Me_2}{Ge}{-}\overset{Me_2}{Ge}{-}SnMe_3$

3b


$Me_3Sn{-}\overset{Me_2}{Ge}{-}\overset{Me_2}{Ge}{-}\overset{Me_2}{Ge}{-}SnMe_3$

3c

2.2. NMR spectroscopic results

2.2.1. General

NMR data of the compounds **1**–**4** and **1a**–**4a** are compiled in Table 1. There is reasonable agreement with most data given in the literature. The values $^1J(^{119}Sn, ^{29}Si)$ and $^2J(^{119}Sn, ^{117}Sn)$ for compound **2a** have been mixed up [11]. Correct data are given in Table 1. The germanium derivative **3** has been studied recently [9], and data for the other compounds are scattered throughout the literature. Accurate NMR data are now available for all compounds **1**–**4** and **1a**–**4a**. These include the determination of most coupling signs [in the following discussion, the notation of reduced coupling constants $K(A,B) = 4\pi^2\ J(A,B)\ (\gamma_A, \gamma_B h)^{-1}$ is frequently used in order to take care of different signs of magnetogyroscopic ratios γ] and isotope-induced chemical shifts $^1\Delta^{12/13}C(^{119}Sn)$. The chemical shifts, also the new δ ^{73}Ge value (-169) for **3a**, are found in the expected regions [14]. The fairly broad ^{73}Ge resonance of **3a** ($h_{1/2} = 180 \pm 10$ Hz) precludes the measurement of' $^1J(^{119}Sn, ^{73}Ge)$, in contrast to the case of **3** where the ^{73}Ge-NMR signal is very sharp as a result of T_d symmetry in solution [9]. The ^{119}Sn-NMR spectrum of **4** shows a B_0-dependent pattern of an AB_2 type spin system for the isotopomer containing three ^{119}Sn, one central ^{119}Sn and two adjacent ^{119}Sn nuclei, the assignment of which was confirmed by calculation.

2.2.2. Coupling constants

The reduced coupling constants $^1K(^{119}Sn,M)$ ($M = {}^{13}C, {}^{29}Si, {}^{73}Ge, {}^{117}Sn$) were found to be positive. This sign was determined here for the first time for the compounds **1**, **1a**, **2**, **2a** and **4**, using 2D heteronuclear shift correlations (HETCOR) of the type $M/^1H$ which allow for the comparison of the signs of $^2K(^{119}Sn, {}^1H_{SnMe})$ (<0) and $^1K(^{119}Sn,M)$ [15] (see Fig. 1). Although a positive sign of $^1K(^{119}Sn,M)$ could have been predicted on the basis of other data for comparable compounds [1, 2, 9, 14a,b], firm experimental evidence is now available which is particularly important in the case of **4** where the sign of $^1K(^{119}Sn, ^{117}Sn)$ is difficult to predict. The comparison of the $^1K(^{119}Sn,M)$ values shows that the data for M = Si and Ge are very similar, although one would have expected a significantly greater value for M = Ge [9] considering the changes in

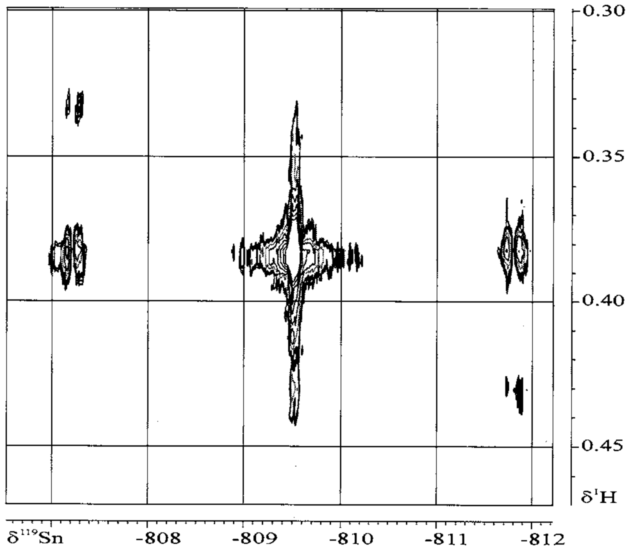


Fig. 1. Contour plot of the 2D 186.5 MHz $^{119}Sn/^1H$ HETCOR experiment [based on $^3J(^{119}Sn,Sn,C, ^1H) = 15.0$ Hz} for $(Me_3Sn)_4Sn$ (**4**), observing the ^{119}Sn signal of the central tin atom. The polarization transfer from ^1H (active nucleus) across $^{117/119}Sn$ (passive nuclei) to the central ^{119}Sn (active nucleus) enables one to compare the signs of $^2K(^{117/119}Sn,C, ^1H)$ and $^1K(^{119}Sn, ^{117/119}Sn)$. The negative tilt of the relevant cross peaks indicates opposite signs. Since the sign of $^2K(^{117/119}Sn,C, ^1H)$ for methyl tin compounds is known to be negative [25], the sign of $^1K(^{119}Sn, ^{117/119}Sn)$ is positive.

Table 1
NMR parameters for the trimethylstannyl element compounds **1**–**4**, **1a**–**4a** and **3b**

Number (M)	δM $^{1}J(^{119}$Sn–M)-[…] [a], $^{2}J(^{13}$C–M)-{…}, $^{1}J(^{13}$C–M)-(…)	δ^{119}Sn $^{2}J(^{119}$Sn–^{117}Sn)-[…] [a]	δ^{13}C(Sn–Me) $^{1}J(^{119}$Sn–^{13}C)-[…] [a], $^{3}J(^{119}$Sn–^{13}C)-{…}	$\delta^{13}\mathrm{C}_{(\mathrm{M-Me})}$ $^{2}J(^{119}$Sn–^{13}C) […]	$^{1}\Delta^{12/13}\mathrm{C}(^{119}\mathrm{Sn})$	$\lvert\Psi(0)\mathrm{M}\rvert^{2}$ a.u. [b]
1 (^{13}C)	−26.4 [−108.3] [+9.4] {3.5}	+49.3 [−309.6] [−19.07]	−3.3 [−316.3] [+27.5] {−11.9}		−15.6 (Me) −24.0 (C)	2.7715
2 (^{29}Si)	−172.0 [+227.1] [+24.6] {4.9}	−34.1 [−33.8] [−2.08]	−6.7 [−365.1] [+23.0] {11.1}		−24.1	3.8105
3 (^{73}Ge)	−515.2 [+37.0] [+23.4]	−25.1 [−42.3] [−2.60]	−6.0 [−258.3] [+22.5] {−11.8}		−20.9	9.5433
4 (^{117}Sn)	−809.5 [+873.3] [+52.1]	−81.5 [+19.4] [+1.19]	−6.0 [−240.5] [+20.9] {11.5}		−15.1	12.6795
1a (^{13}C)	+9.8 [−340.1] [+29.6]	−30.2 [+18.4] [+1.13]	+11.2 [−297.8] [+25.9] {5.0}	+25.9 [+18.3]	−16.5	2.7715
2a (^{29}Si)	−38.2 [+504.0] [+54.4] {5.7} (−37.0)	−99.0 [+704.1] [+43.4]	−11.3 [−248.5] [+21.6] {10.2}	−2.7 [−26.0]	−28.4	3.8105
3a (^{73}Ge)	−169.0	−73.2 [+706.6] [+43.5]	−10.3 [−249.8] [+21.7] {11.9}	−3.3 [−22.8]	−24.7	9.5433
3b [c] (^{73}Ge)	−133.2	−79.5 [296.3] [d] [18.2]	−10.2 [−247.9] [+21.6]	−3.4 [+30.1] {8.3} [e]	−25.2	9.5433
4a [f] (^{117}Sn)	−261.7 [2873] [176.9] {44.1} (179.4)	−99.5 [763] [47.0]	−9.2 [238.4] [+20.7]	−14.0 [25.0]	Not reported	12.6795

[a] The second value in [ ] refers to the reduced coupling constant $^{1}K(^{119}\mathrm{Sn,M}) = 4\pi^{2}\ {}^{1}J(^{119}\mathrm{Sn,M})\ [\gamma(^{119}\mathrm{Sn})\ \gamma(\mathrm{M})\ h]^{-1}$.

[b] Calculated valence s electron densities [24].

[c] **3b**: δ^{1}H [$J(^{119}$Sn, ^{1}H)] = 0.36 [48.6] $\mathrm{Me_3Sn}$; 0.60 [31.2] $\mathrm{Me_2Ge}$. **3c**: δ^{13}C = −10.2 $\mathrm{Me_3Sn}$; −4.8 $\mathrm{Me_2Ge}$–Sn; −3.2 $\mathrm{Me_2G}$; δ^{1}H [$J(^{119}$Sn,^{1}H)] = 0.36 [48.6] $\mathrm{Me_3Sn}$; 0.54 $\mathrm{Me_2Ge}$; 0.65 [30.5] $\mathrm{Me_2Ge}$–Sn; δ^{119}Sn = −80; δ^{73}Ge = −118 central Ge, −133 $\mathrm{GeMe_2}$–Sn.

[d] $^{3}J(^{119}$Sn–^{117}Sn).

[e] $^{3}J(^{119}$Sn–^{13}C).

[f] Data from T.N. Mitchell, G. Walter, J. Chem. Soc. Perkin Trans. 2 (1977) 1842.

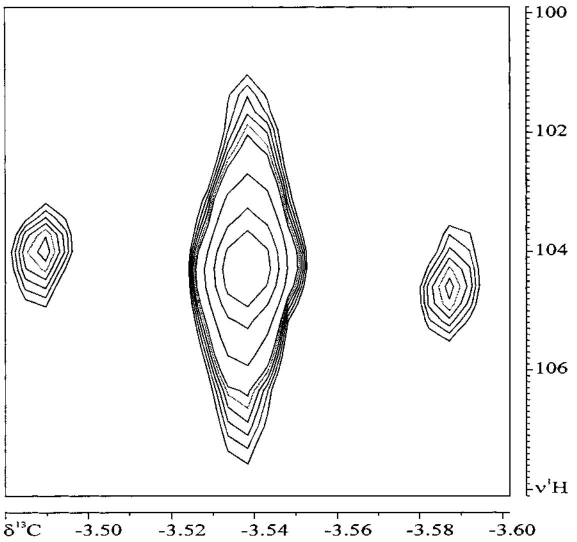


Fig. 2. Contour plot of the $^{13}C/^{1}H$ HETCOR experiment for the methyl groups in $(Me_3Sn)_4C$ (**1**), based on $^{1}J(^{13}C,^{1}H)$, showing the part of the $^{117/119}Sn$ satellites due to $^{3}J(^{117/119}Sn,C,Sn,^{13}C)$. Note the slightly negative tilt of the cross peaks which (i) allow to measure accurately the magnitude of otherwise unresolved $^{4}J(^{117/119}Sn,C,Sn,C,{}^{1}H) = 0.6$ Hz, and (ii) enables one to determine opposite signs of $^{4}K(^{117/119}Sn,C,Sn,C,{}^{1}H)$ and $^{3}K(^{117/119}Sn,C,Sn,{}^{13}C)$.

the calculated valence s electron densities $|\Psi_0(M)|^2$ (see Table 1). Knowing that $^{1}K(^{119}Sn,{}^{117}Sn)$ in **4** is positive, the change in the magnitude of $^{1}K(^{119}Sn,M)$ for M = ^{73}Ge and ^{117}Sn follows roughly the ratio of the respective valence s electron densities $|\Psi_0(M)|^2$. Thus, the situation for M = Si and Ge indicates that there are increasingly negative contributions to $^{1}K(^{119}Sn,^{73}Ge)$ in **3** which arise from the Sn–Ge bonds and that similar effects are also operating in the case of the Sn–Sn bonds in **4**.

The sign of geminal coupling constants is known to change readily as a result of the nature of the intervening atom because of geometrical factors and the influence exerted by substituents at the intervening atom [16]. This is evident in both series **1**–**4** and **1a**–**4a**. The sign of $^{2}K(^{119}Sn,^{117}Sn)$ changes from negative (**1**–**3**) to positive (**4**), whereas it stays positive in **1a** to **4a**. In the latter series, the sign of $^{2}K(^{119}Sn,^{13}C)$ is negative in **1a** but positive in **2a** to **4a**. These signs were determined either by 2D HETCOR experiments, taking advantage of polarization transfer based on small long-range coupling constants $^{4}J(^{119}SnMSnC,^{1}H)$ [17] (see Fig. 2 for accurate measurement of such long-range coupling constants), or by selective 1D heteronuclear triple resonance experiments of the type $^{119}Sn\{^{1}H,^{13}C\}$ in which ^{13}C transitions in the $^{119}Sn,^{117}Sn,^{13}C$ spin system are irradiated [9] in order to observe effects from spin tickling [18] (Fig. 3). The two-bond indirect nuclear spin-spin coupling between nuclei with an open s-shell electron configuration across a tetrahedral center in the absence of lone pairs of electrons should in principle be described by a negative ^{2}K [16]. Any deviation from this prediction such as in **4**, **1a**–**4a**, and **2a**–**4a** must be traced to the influence of polarizable Sn-element bonds and possibly geometrical effects. The latter effects can be discarded for the compounds studied here by looking at the data [$^{1}K(^{119}Sn,^{117}Sn) > 0$; $^{2}K(^{119}Sn,^{117}Sn) > 0$, $^{2}K(^{119}Sn,Sn,^{13}C) > 0$] for a 1,2,3-tristanna-[3]ferrocenophane **4b**. Its molecular structure has been determined by X-ray structural analysis which reveals that the angles SnSnSn [107.0(1) and 107.5(1)°] are close to the tetrahedral angle [19]. Therefore, the nature of the Sn–M bonds must be responsible. In particular, the Sn–Si, Sn–Ge and Sn–Sn bonding MO's have antibonding counterparts of low energy. The magnetic field induced mixing of these energy levels with ground states creates contributions which eventually cause a sign change in the respective one- and/or two-bond

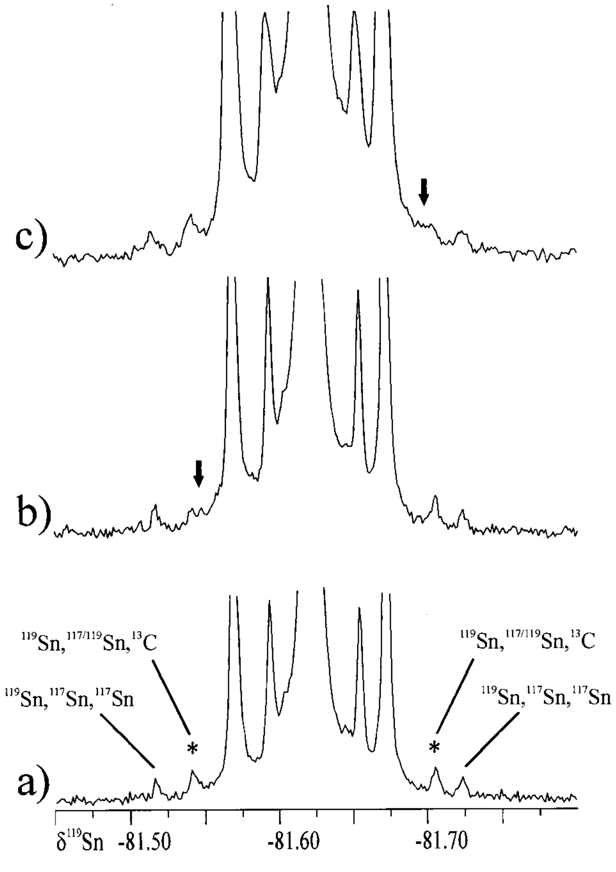
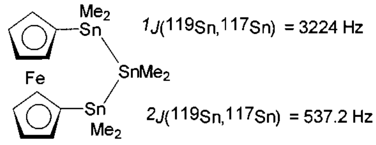


Fig. 3. Selective ^{13}C spin tickling experiments, observing the ^{1}H-decoupled 186.5 MHz ^{119}Sn-NMR spectrum of $(Me_3Sn)_4Sn$ (**4**). Effects of tickling are marked by arrows. (a) Normal $^{119}Sn\{^{1}H\}$-NMR spectrum; the signals of the relevant isotopomer containing ^{119}Sn, $^{119/117}Sn,^{13}C$ are marked with asterisks (b) $^{119}Sn\{^{1}H,^{13}C\}$ experiment; effects of selective low power irradiation of low field ^{13}C transitions. (c) $^{119}Sn\{^{1}H,^{13}C\}$ experiment; effects of selective low power irradiation of high field ^{13}C transitions.

coupling constants. The remarkable sensitivity of $^2J(^{119}Sn,^{117}Sn)$ towards apparently small structural changes can be seen in the cases of **1** (−309.6 Hz) and **1a** (+18.4 Hz). The vicinal coupling constants $^3K(^{119}Sn,^{13}C)$ are positive and of similar magnitude, as expected for a Karplus-type dihedral dependence [20]. In the case of **3b**, the coupling constant $^3J(^{119}Sn,Ge,Ge,^{117}Sn) = 296.3$ Hz can be measured; attempts to determine its sign failed. However, following the trend of vicinal coupling constants, a positive sign can be assumed. The magnitude is in the range observed for comparable bis(trimethylstannyl)alkanes [21].



4b

2.2.3. *Isotope induced chemical shifts $^1\Delta^{12/13}C(^{119}Sn)$*

In the frame of a simplified approach, a negative sign of $^1\Delta^{12/13}C(^{119}Sn)$ can be predicted, i.e. the magnetic shielding of the ^{119}Sn nuclei in the heavy isotopomer is increased with respect to the lighter one. This is indeed true for the compounds studied here. The value $^1\Delta^{12/13}C(^{119}Sn)$ for the central carbon atom in **1** (−24 ppb) is still an isolated value. However, numerous data $^1\Delta^{12/13}C_{Me}(^{119}Sn)$ are available for Me_3Sn groups [4–6]. The strong dependence of isotope induced chemical shifts on electronic terms (in comparison to mass dependent dynamic factors) [22] means that one-bond coupling constants which are dominated purely by electronic terms should help to explain changes in the magnitude of $^1\Delta^{12/13}C_{Me}(^{119}Sn)$. There is evidence for a crudely linear relationship between the magnitude of $|^1J(^{119}Sn, ^{13}C_{Me})|$ and $^1\Delta^{12/13}C_{Me}(^{119}Sn)$ [4] [even a change of the sign of $^1\Delta^{12/13}C_{Me}(^{119}Sn)$ is observed if the magnitude of $|^1J(^{119}Sn,^{13}C)|$ exceeds 400 Hz]. This trend is supported by the inspection of the data for **1** and **2** or **1a** and **2a**. However, other data pairs (e.g. for **1** and **4** or **2a** and **3a**) do not seem to fit very well into this concept. This indicates that electronic terms influence $^1\Delta^{12/13}C(^{119}Sn)$ and $|^1J(^{119}Sn,^{13}C)|$ in a slightly different way. Influences arising from easily polarizable Sn-element bonds of the magnitude of $^1J(^{119}Sn, ^{13}C_{Me})$ may not be reflected in $^1\Delta^{12/13}C_{Me}(^{119}Sn)$ There are still more data needed in order to make better use of the isotope induced chemical shifts $^1\Delta^{12/13}C(^{119}Sn)$.

3. Experimental

3.1. *General*

All compounds were synthesized and handled under Ar atmosphere, using carefully dried glassware and dry solvents. The compounds **1**–**3**, **1a** [10], **2a** [11] were prepared according to literature procedures.

NMR spectra were measured from samples (ca. 10% in C_6D_6 at 25°C) in 5 mm (o.d.) tubes using Bruker ARX 250 and DRX 500 spectrometers. Polarization transfer experiments were optimized by using INEPT pulse sequences [23] Chemical shifts are given relative to Me_4Si [δ^1H $(C_6D_5H) = 7.15$, $\delta^{13}C$ $(C_6D_6) = 128.0$], Me_4Ge [$\delta^{73}Ge = 0$ for Ξ $(^{73}Ge) = 3.488315$ MHz], Me_4Sn [$\delta^{119}Sn = 0$ for $\Xi(^{119}Sn) = 37.290665$ MHz]. Heteronuclear triple resonance experiments $^{119}Sn\{^1H,^{13}C\}$ were carried out with the DRX 500 instrument (three independent frequency channels), using a triple resonance probehead tuned selectively to ^{13}C and tuneable to various X nuclei. Filters available for ^{31}P serve adequately for ^{119}Sn. EI-MS (70 eV): Varian MAT CH7 with direct inlet.

3.2. *Bis(trimethylstannyl)dimethylgermane **3a***

Compound **3a** was prepared following the procedure described for **2a**. However, **3a** was obtained in a mixture with 1,2-bis(trimethylstannyl)tetramethyldigermane **3b** and 1,3-bis(trimethylstannyl)hexamethyltrigermane **3c** of which it could not be completely separated. Distillation gave $Me_3SnSnMe_3$ in the first fraction followed by a second fraction [b.p. 70°C/0.01 Torr] which contained **3a**, **3b** and **3c** in a ratio of 10:3.8:2.8, respectively. Further attempts at separation by distillation did not change the composition to an appreciable extent. EI-MS (70 eV): *m*/*e* (%): 326 (65) $M^+ - 104$; 265 (20) $M^+ - 165$ (**3a**); 369 (30) $M^+ - 165$ (**3b**); 636 (18) M^+, 471 (50) $M^+ - 165$ (**3c**); 738 (30) M^+, 575 (45) $M^+ - 165$ [$Me_3Sn(GeMe_2)_3SnMe_3$; clear evidence for this compound from NMR spectra is missing].

3.3. *Tetrakis(trimethylstannyl)tin **4***

Trimethyltin chloride (10 g, 0.05 mol) was dissolved in THF (20 ml) and added dropwise within 1 h to 10 g of freshly cut pieces of lithium in 50 ml of THF at 0°C. After 12 h at 22°C, THF was removed in vacuo at room temperature. This process was stopped as soon as there was no longer any liquid visible in the flask, but only a solid, black residue. This residue was extracted three times with about 30 ml of pentane each time. After evaporation of pentane from the extract, the flask contained 0.6 g of crystals mixed with a yellow oil. This residue was then dissolved in THF and cooled at −40°C. A solution of trimethyltin chloride (0.2 g) in THF (20 ml) was added dropwise within 2 h. This mixture was stirred for 3 h at −40°C, then warmed to room temperature and stirred for 12 h. After removing all volatile material in vacuo, a yellow solid (dec.

$>90°C$) was obtained (0.5 g, 5%) which was identified as pure ($>90\%$) **4**. EI-MS (70 eV): m/e (%): 738(38) M^+, 693(39) $M^+ - 45$, 57(100) $C_4H_9^+$.

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