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# Deconvoluting Steric and Electronic Substituent Effects on the Properties of Linear Oligostannanes: Synthesis and Characterization of a New Series Incorporating the $Bu^t{}_2Sn$ Group

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The synthesis and full characterization, including detailed $^{119}Sn$ NMR analysis, of the new series of oligostannanes $X{-}Bu^n{}_2Sn{-}[Bu^n{}_2Sn]_m{-}Bu^t{}_2Sn{-}[Bu^n{}_2Sn]_n{-}SnBu^n{}_2CH_2CH_2OEt$ (**1a**, X = 2-ethoxyethyl, $m = n = 0$; **2a**, X = $Bu^n$, $m = 0$, $n = 1$; **3a**, X = 2-ethoxyethyl, $m = n = 1$; **4a**, X = $Bu^n$, $m = 1$, $n = 2$; **5a**, X = 2-ethoxyethyl, $m = n = 2$; **6a**, X = 2-ethoxyethyl, $m = n = 3$) that incorporate a single $Bu^t{}_2Sn$ group are reported. Comparison of this new spectroscopic database, in particular, electronic spectra and $^{119}Sn$ NMR parameters, with those obtained for known analogous per-*n*-butylated derivatives, including the three compounds $EtOCH_2CH_2Bu^n{}_2Sn{-}[Bu^n{}_2Sn]_n{-}SnBu^n{}_2CH_2CH_2OEt$ (**1c** ($n = 1$), **2c** ($n = 2$), and **3c** ($n = 3$)), which are prepared for the first time in pure form, suggest that **1a**−**6a** are free of structural distortions caused by steric interactions between substituents on adjacent tin atoms. Accordingly, dramatic perturbations that are observed in the $^1J(^{119}Sn{-}^{119}Sn)$ values for Sn−Sn bonds that incorporate the $Bu^t{}_2Sn$ group in these compounds, relative to the per-*n*-butyl derivatives, are proposed to arise from an electronic effect of the *tert*-butyl substituent.

## Introduction

The unique optical properties of linear group 14 polymetallanes of the general formula $X{-}[R_2M]_n{-}X$ (M = Si, Ge, and Sn) have been of considerable interest for the past 30 years.[1−4] In this respect, oligomers of discrete chain length, and more recently of restricted conformation, have played a major role in helping to elucidate electronic structure and, thereby, the origins of these properties.[3,4] However, in this pursuit, many outstanding issues still remain to be fully addressed. One, for example, is that while it is well-known that the nature of the organic group R can dramatically alter the physical properties of polymetallanes, little has been done to deconvolute contributions made from both the steric and electronic effects of a given substituent in order to develop guiding principles for their use. Certainly, part of this problem lies with the controversy that still surrounds the validity of assigning different field effects to the various commonly used alkyl substituents, i.e., methyl, ethyl, 1-methylethyl ($Pr^i$), and 1,1-dimethylethyl ($Bu^t$).[5] Regarding polymetallanes, sometime ago, Mitchell and Walter[6] proposed that there existed a correlation between the values for the valence-electron-mediated indirect one-bond coupling constants $^1J(^{119}Sn{-}^{119}Sn)$ for the Sn−Sn bonds in di- and tristannanes and $\Sigma\sigma^*$, the sum of the Taft constants, $\sigma^*$, for the various attached alkyl substituents. Since a larger reduction in $^1J(^{119}Sn{-}^{119}Sn)$ was observed for alkyl substituents that had an increased degree of branching, cf., a value of (+)4462 Hz in $Me_3SnSnMe_3$ vs (+)780 Hz in $Pr^i{}_2Bu^tSnSnBu^tPr^i{}_2$, it was suggested that the basis for this was an electronic effect on $\psi_{(Sn)}{}^2(0)$, the s-electron density at the tin nuclei, and interestingly,

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(1) For a general review of polysilanes, see: Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359−1410.

(2) For recent studies of high molecular weight group 14 polymetallanes, see: (a) Devylder, N.; Hill, M.; Molloy, K. C.; Price, G. J. *J. Chem. Soc., Chem. Commun.* **1996**, 711−712. (b) Fossum, E.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 1618−1625. (c) Imori, T.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1993**, 1607−1609. (d) Imori, T.; Lu, V.; Cai, H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 9931−9940. (e) Jones, R. G.; Benfield, R. E.; Evans, P. J.; Swain, A. C. *J. Chem. Soc., Chem. Commun.* **1995**, 1465−1466. (f) Lu, V.; Tilley, T. D. *Macromolecules* **1996**, *29*, 5763−5764. (g) Mochida, K.; Chiba, H. *J. Organomet. Chem.* **1994**, *473*, 45−54. (h) Takeda, K.; Shiraishi, K. *Chem. Phys. Lett.* **1992**, *195*, 121−126. (i) Yokoyama, Y.; Hayakawa, M.; Azemi, T.; Mochida, K. *J. Chem. Soc., Chem. Commun.* **1995**. (j) Reichl, J. A.; Popoff, C. M.; Gallagher, L. A.; Remsen, E. E.; Berry, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 9430−9431. (k) Babcock, J. R.; Sita, L. R. *J. Am. Chem. Soc.* **1996**, *118*, 12481−12842.

(3) For recent studies of oligosilanes, see: (a) Albinsson, B.; Teramae, H.; Downing, J. W.; Michl, J. *Chem. Eur. J.* **1996**, *2*, 529−538. (b) Albinsson, B.; Teramae, H.; Plitt, H. S.; Goss, L. M.; Schmidbauer, H.; Michl, J. *J. Phys. Chem.* **1996**, *100*, 8681−8691. (c) Imhof, R.; Teramae, H.; Michl, J. *Chem. Phys. Lett.* **1997**, *270*, 500−505. (d) Maziéres, S.; Raymond, M. K.; Raabe, G.; Prodi, A.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 6682−6683. (e) Obata, K.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **1997**, *119*, 11345−11346.

(4) For oligostannanes with $n > 4$, see: (a) Creemers, H. M. J. C.; Noltes, J. G. *J. Organomet. Chem.* **1967**, *7*, 237−247. (b) Jousseaume, B.; Chanson, E.; Bevilacqua, M.; Saux, A.; Pereyre, M.; Barbe, B.; Petraud, M. *J. Organomet. Chem.* **1985**, *294*, C41−C45. (c) Adams, S.; Dräger, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1255−1256; *Main Group Met. Chem.* **1988**, *XI*, 151−180. (d) Sita, L. R. *Organometallics* **1992**, *11*, 1442−1444. (e) Sita, L. R.; Terry, K. W.; Shibata, K. *J. Am. Chem. Soc.* **1995**, *117*, 8049−8050. (f) Sita, L. R.; Shibata, K. In *Modular Chemistry*; NATO ASI Series C; Michl, J., Ed.; Kluwer Academic Publishers: Boston, 1997; Vol. 499, pp 587−599.

(5) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1985; p 235 and references therein.

(6) Mitchell, T.; Walter, G. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1842−1847.

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these authors speculated that this electronic effect should materialize as a negative $^1J(^{119}Sn-^{119}Sn)$ value in $Bu^t{}_3Sn-SnBu^t{}_3$.[7,8] Kennedy and co-workers[9] argued, however, that the range of magnitudes observed was too large for this to be the main factor; thus, a more likely explanation was that due to Sn−Sn bond elongation that arises from nonbonded steric interactions between bulky substituents on adjacent tin atoms, a reduction in $\beta$, the s-orbital overlap integral for the Sn−Sn bond, occurs so that negative contributions to $\pi_{SnSn}$, the mutual polarizability term in the Fermi contact component of $^1J$, become significant and lead to an observed reduction.[10] More recently, Adams and Dräger[4c] reported the structures, electronic spectra, and $^{119}Sn$ NMR parameters for the oligostannane series $Ph_3Sn-[Bu^t{}_2Sn]_n-SnPh_3$ ($n = 1-4$), which is characterized in the solid state by increasingly larger Sn−Sn bond length and Sn−Sn−Sn bond angle distortions as chain length increases. On the basis of a correlation of Sn−Sn bond length and $^1J(^{119}Sn-^{119}Sn)$ values found for this series, these authors hypothesized that a change in the sign of the latter parameter, from positive to negative, occurs at a Sn−Sn bond distance of 2.85 Å and that this correlation actually applies, in general, to all polystannane frameworks.[11,12] Finally, Herberhold and coworkers[13] have experimentally determined the sign and magnitude of $^1J(^{207}Pb-M)$ ($M = {}^{119}Sn$ and $^{207}Pb$) in the unsymmetric dimetallanes and diplumbanes $Bu^t{}_3Pb-SnR_3$ ($R = Me$, Et, $Bu^n$, $Bu^t$, and Ph) and $Bu^t{}_3Pb-PbR_3$ ($R = Me$, Et, $Pr^i$, *n*-hexyl, and c-hexyl) and found all of these coupling constants to be large and their corresponding reduced coupling constants, $^1K$, to be negative.[8] Given this, these authors conclude that "the high polarizability of the lead atom causes a small s overlap, and together with the influence of relativistic effects,[14] this enforces the inversion of signs of coupling constants involving the $^{207}Pb$ nucleus and other nuclei with an open shell valence electron configuration".[10c] Thus, at the present time, regarding one-bond coupling involving the heaviest group 14 elements, tin and lead, in polymetallanes, three different influences on the sign and magnitude of this coupling have been proposed: (1) an electronic influence of the organic substituents, (2) a steric influence of these substituents brought about by strong nonbonded interactions between them on adjacent metal atoms, and (3) an intrinsic nuclear property of these heavy elements. Unfortunately, as can be seen, all of the above arguments are based on oligostannane and diplumbane derivatives, which can be considered as being "sterically encumbered", and therefore, it is not possible to separate the two different types of substituent contributions, if indeed two do exist, nor to subtract these contributions from the intrinsic nuclear properties of the heavy elements. Thus, to further investigate the possible influence of substituent electronic effects on heavy-atom polymetallanes, and in particular, on oligostannanes, we set out to synthesize and characterize a new series of derivatives of the latter that incorporate a single $Bu^t{}_2Sn$ moiety but which are still free of Sn−Sn bond length distortions, and to compare this new database of properties with that of known per-*n*-butylated derivatives.[4b,d,e] Herein, we report the successful results of this effort which has provided the new oligostannanes, **1a**−**6a**, **1c**−**3c**, and **1d** for study (see Figure 1). Further, preliminary studies reported here show that the *electronic* effects of the *tert*-butyl group do indeed appear to have a profound influence on the nuclear magnetic properties of oligostannanes and, therefore, by default, on the electronic makeup of these heavy-atom polymetallanes.

## Results and Discussion

**Synthesis.** The route taken to the originally desired oligostannanes **1a**, **3a**, **5a**, and **6a** is shown in Scheme 1, and it is based on synthetic methodology developed earlier for the synthesis of the oligostannane series $Bu^n{}_3Sn-[Bu^n{}_2Sn]_n-SnBu_2-CH_2CH_2OEt$ ($n = 1-4$; **1b**−**4b**, respectively).[4d] While on paper this looked to be an efficient process by which to access fairly long oligostannanes, in reality, progress was slowed considerably by having to resolve synthetic difficulties that were apparently not present (or not as severe) in the prior syntheses. As will be noted, however, one benefit of these difficulties was the formation of the fortuitous byproducts **1d**, **2a**, and **4a** that result from a as-of-yet undetermined *n*-butyl group metathesis process.

To begin, as Scheme 1 shows, reaction of 2 equiv of the reagent, di(*n*-butyl)(dimethylamino)(2-ethoxyethyl)stannane (**7**) with bis(1,1-dimethylethyl)stannane (**8**) in hexane provided a 82% yield of the desired tristannane **1a** after purification by column chromatography on silica gel under an inert atmosphere. As with all of the syntheses of the oligostannanes, the key to obtaining highly pure products resides with the 2-ethoxyethyl substituent which has favorable chromatography characteristics and, thus, allows one to effectively fractionate even fairly complex product mixtures. It can also be noted that for **1a**, the reaction shown in Scheme 1 can be successfully scaled to provide large multigram quantities without an apparent sacrifice in yield.

In contrast to the facile preparation of **1a**, synthesis of the pentastannane **3a** proved to be much more challenging. More specifically, in the previous syntheses of **1b**−**4b**, diisobutylaluminum hydride (DIBAL-H) was used to quantitatively remove the 2-ethoxyethyl group to provide a new Sn−H functionality that was

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[7] Tin has two $I = {}^1/_2$ isotopes, $^{119}Sn$ and $^{117}Sn$, that have relatively high natural abundances, 8.58% and 7.61%, respectively. For magnetically equivalent tin atoms, $^nJ(^{119}Sn-^{119}Sn)$ is derived from the relationship: $^nJ(^{119}Sn-^{119}Sn)/^nJ(^{119}Sn-^{117}Sn) = 1.046$.

[8] Strictly speaking, any meaningful discussion of the magnitude and sign of the indirect one-bond coupling between two nuclei, A and B, should be made with respect to the reduced coupling constant, which is defined as $^1K_{AB} = (4\pi^2/h)^1J_{AB}(\gamma_A\gamma_B)^{-1}$. For heteronuclear coupling ($A \neq B$), this eliminates the problem where the magnetogyric ratios of the two nuclei, $\gamma_A$ and $\gamma_b$, are of opposite sign. For homonuclear coupling ($A = B$), however, it is easy to see that the sign of $^1J$ bears directly on the coupling mechanism.

[9] Kennedy, J. D.; McFarlane, W.; Pyne, G. S.; Wrackmeyer, B. *J. Chem. Soc., Dalton Trans.* **1975**, 386−390.

[10] (a) Ramsey, N. F. *Phys. Rev.* **1953**, *91*, 303. (b) Pople, J. A.; Santry, D. P. *Mol. Phys.* **1964**, *8*, 1−18. (c) Jameson, C. J.; Gutowsky, H. S. *J. Chem. Phys.* **1969**, *51*, 2790−2803.

[11] The signs of $^1J(^{119}Sn-^{119}Sn)$ for $Ph_3Sn-(Bu^t{}_2Sn)_n-SnPh_3$ ($n = 1-4$) were not experimentally determined.

[12] For databases of $^{119}Sn$ NMR parameters for di-, tri-, and some additional tetrastannanes, as well as other polystannane frameworks, see ref 4c and (a) Wrackmeyer, B. *Ann. Rep. NMR Spectrosc.* **1985**, *16*, 73−186. (b) Sita, L. R. *Adv. Organomet. Chem.* **1995**, *38*, 189−243.

[13] Herberhold, M.; Tröbs, V.; Wrackmeyer, B. *J. Organomet. Chem.* **1997**, *541*, 391−400.

[14] (a) Pyykkö, P. *Chem. Phys.* **1977**, *22*, 289−296. (b) Pyykkö, P.; Wiesenfeld, L. *Mol. Phys.* **1981**, *43*, 557−580. (c) Pyykkö, P. *J. Organomet. Chem.* **1982**, *232*, 21−23.

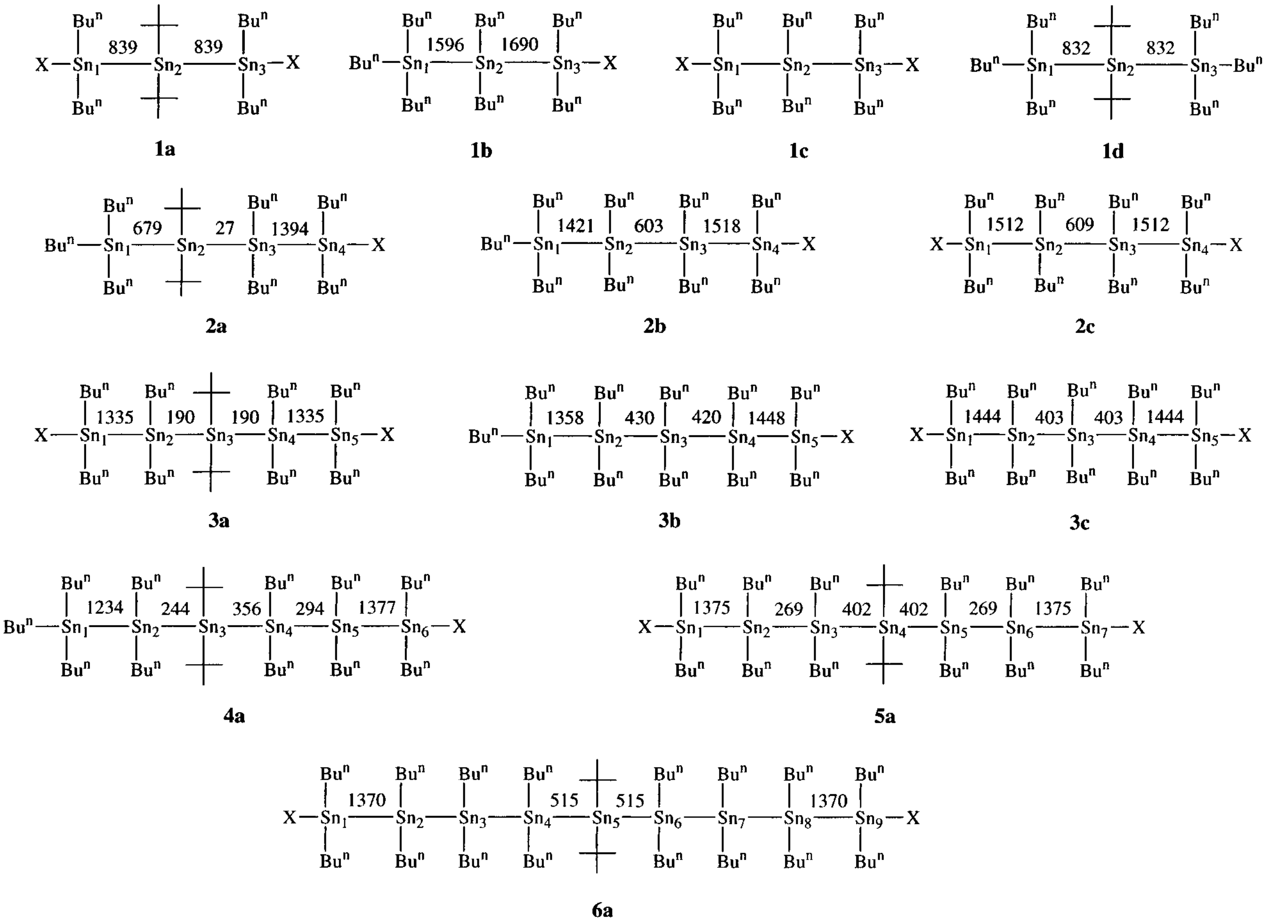

**Figure 1.** Structures and atom-numbering schemes for the new oligostannanes. Absolute values for $^1J(^{119}Sn-^{119}Sn)$ coupling constants are shown above their respective Sn−Sn bonds. X = 2-ethoxyethyl.

then reacted with **7** to effect chain-length extension. Unfortunately, when applied in the present case, reaction of **1a** with 2 equiv of DIBAL-H, followed by a procedure to remove the DIBAL-OEt that is formed, provided an intermediate product that when reacted with 2 equiv of **7**, resulted in only a 8% yield of the desired product **3a** after column chromatography. From this purification step, however, two additional fractions were also obtained, and these proved to be the tristannane **1d** and the tetrastannane **2a**, which were isolated in respective yields of 28% and 14%. Originally, it was believed that both of these latter coproducts possessed 3-methylpropyl (isobutyl) end groups that might have arisen from cross metathesis involving an isobutyl group from DIBAL-X (X = H or OEt) and the Sn−H terminal functionality. However, subsequent results suggested this not to be the case. That is, to eliminate the possibility that cross metathesis with a DIBAL-based compound was occurring, a different class of deprotection reagent was sought, and while this proved to be more difficult than anticipated, it was eventually found that alane ($AlH_3$), prepared by the in-situ reduction of zinc bromide by lithium aluminum hydride ($LiAlH_4$) in diethyl ether,[15] could be utilized for the intended purpose. Now, using this reagent in place of DIBAL-H, an increased yield of **3a** (30% yield) was indeed obtained, however, this was achieved along with a surprising increase in the amount of **2a** (30% yield) but a smaller yield of the tristannane **1d** (19%). Clearly, though, this alternative methodology served to eliminate metathesis of an isobutyl group from consideration, and therefore, we now believe the origin of the terminal *n*-butyl groups in **1d** and **2a** may arise from a novel *n*-butyl group metathesis process involving the key reagent **7**. As will be developed further, why this process materializes in the synthesis of oligostannanes which incorporate the $Bu^t_2Sn$ group may be electronic rather than steric in origin.

With the pure pentastannane **3a** in hand, synthesis of the heptastannane **5a** using $AlH_3$ was attempted next. Satisfactorily, as Scheme 1 shows, **5a**, which is now the longest oligostannane yet to be prepared and isolated in pure form, was obtained in a significantly higher yield (47%). However, column chromatography of the crude product also provided a small amount (4% yield) of the hexastannane **4a**, thereby, indicating that the problematic *n*-butyl metathesis process was still operative but to a much smaller degree. It must also be noted at this point that as oligostannane chain length increases, there appears to be an increased instability of these Sn−Sn-bonded frameworks toward silica-gel chromatography, and thus, repetitive chromatographic separations are to be avoided.

Although an increase in yield in going from the synthesis of **3a** to that of **5a** was achieved, this trend, unfortunately, did not continue in the case of the synthesis of the nonastannane **6a**. Here, it appears that several problems, such as the noted increase in instabil-

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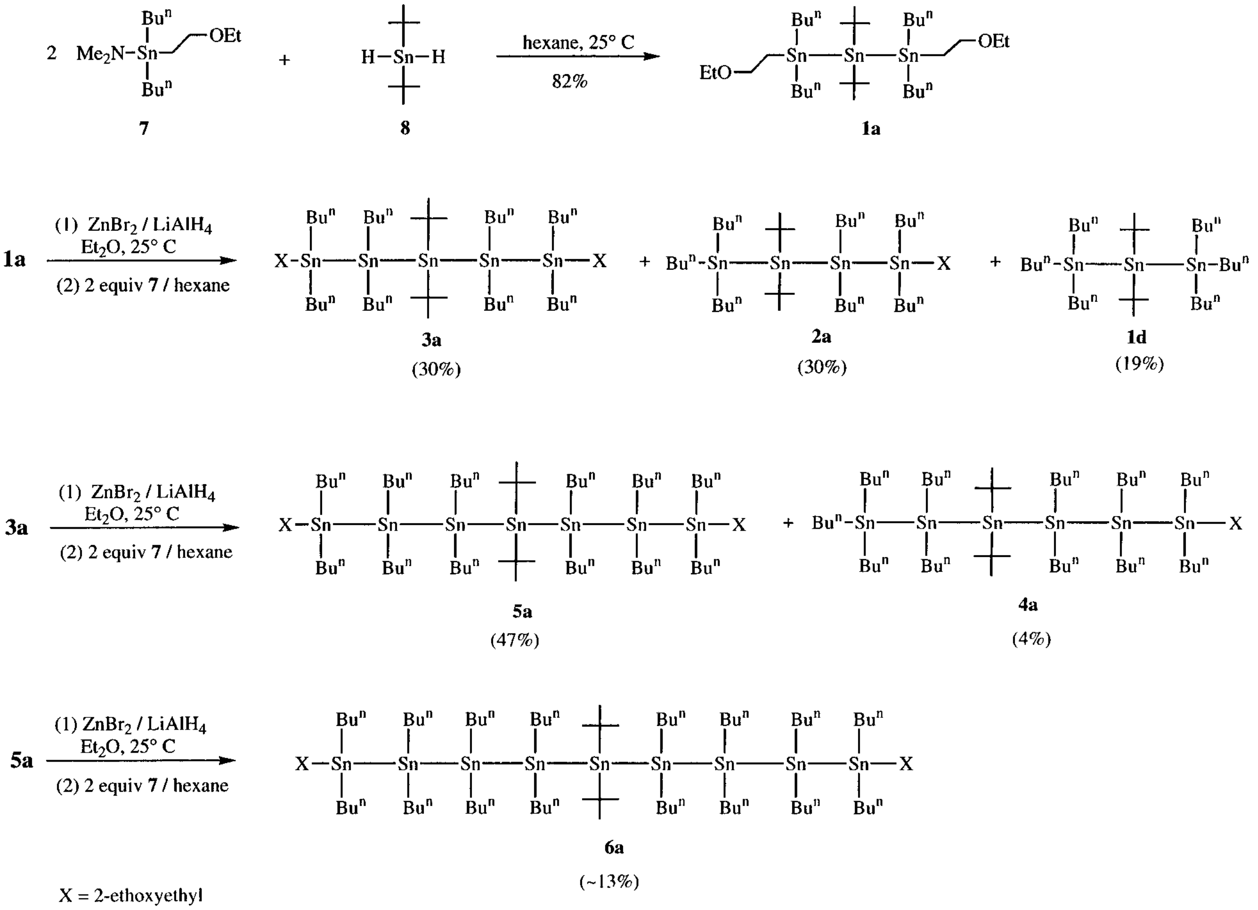
[15] Ashby, E. C.; Sanders, J. R.; Claudy, P.; Schwartz, R. *J. Am. Chem. Soc.* **1973**, *95*, 6485−6486.

**Scheme 1**



ity toward column chromatography, conspire to limit the utility of the synthetic strategy of Scheme 1 for the synthesis of significantly long oligostannanes as it is currently practiced. Hence, our best attempt at preparing **6a** in pure form resulted in a low yield of the desired material (ca. 13%), which was contaminated with a small amount of an inseparable impurity. While this impurity thwarted acquisition of a satisfactory chemical analysis, identification of **6a** as being the major component could nonetheless be unequivocally established through spectroscopic characterization.

Finally, regarding synthesis, it was desirable to have some pure per-*n*-butyl oligostannanes that more closely resemble the *tert*-butyl derivatives for comparison purposes. In this regard, the series of oligostannanes X−[Bu$^n{}_2$Sn]$_n$−X ($X$ = 2-ethoxyethyl, $n$ = 3−15), which includes **1c**−**6c** ($n$ = 3−7 and 9, respectively), have been prepared by an oligomerization process.[4e] This mixture of oligomers was then separated on an analytical scale by high-pressure liquid chromatography (HPLC), and the electronic spectra of the individual components were cataloged by using a diode-array UV−vis detector.[4e] Now, using a strategy similar to Scheme 1, but one employing DIBAL-H for the deprotections, the tristannane **1c** and the pentastannane **3c** were synthesized and obtained in pure form according to Scheme 2. As can be noted, in the synthesis of **1c**, a very small amount of the tetrastannane **2c** was obtained through a side reaction that presumably involves transamination of the reagent **7** with di(*n*-butyl)stannane (**9**) to produce higher order oligomers. Importantly, however, while no attempt was made to optimize the yields for these compounds, which were 53% and 58% for compounds **1c** and **3c**, respectively, no evidence was found for the presence of oligostannanes **1b** and **2b**, which could have resulted from the *n*-butyl group metathesis process that was observed in the synthesis of **1a** and **3a**. Finally, as the amount of tetrastannane **2c** that was obtained as a side product was insufficient for full chemical and spectroscopic analyses, this compound was prepared in a larger quantity by the rational route shown in Scheme 2. Thus, palladium-catalyzed dehydrogenative coupling of di(*n*-butyl)(2-ethoxyethyl)stannane (**10**)[4e] provided the distannane **11** in an excellent yield (89%), and this compound was then subjected to the standard chain homologation sequence to provide the tetrastannane **2c** in modest yield (60%).

**Characterization.** A key feature of the electronic spectra of group 14 polymetallane oligomers is a moderately intense low-energy transition that red shifts with increasing chain length.[1−4] Since for oligostannanes there now appears to be some evidence that perturbations in $\lambda_{max}$ for this transition reflect changes in Sn−Sn bond length,[4c,12b] the electronic spectra for the new compounds reported here were of interest with regard to what they might tell of the steric effects exerted by the −Bu$^t{}_2$Sn− group. Hence, the data obtained from the collection of spectra for **1a**−**6a** (shown in Figure 2), **1c**−**3c**, and **1d** were compared with the corresponding data for the known *n*-butylated analogues **1b**−**4b**[4d] and **4c**−**6c**.[4e] As Table 1 indicates, among all of the derivatives, $\lambda_{max}$ remains virtually unchanged within the 2 nm resolution of the different spectrometers used and even more so between the values for the two

**Scheme 2**

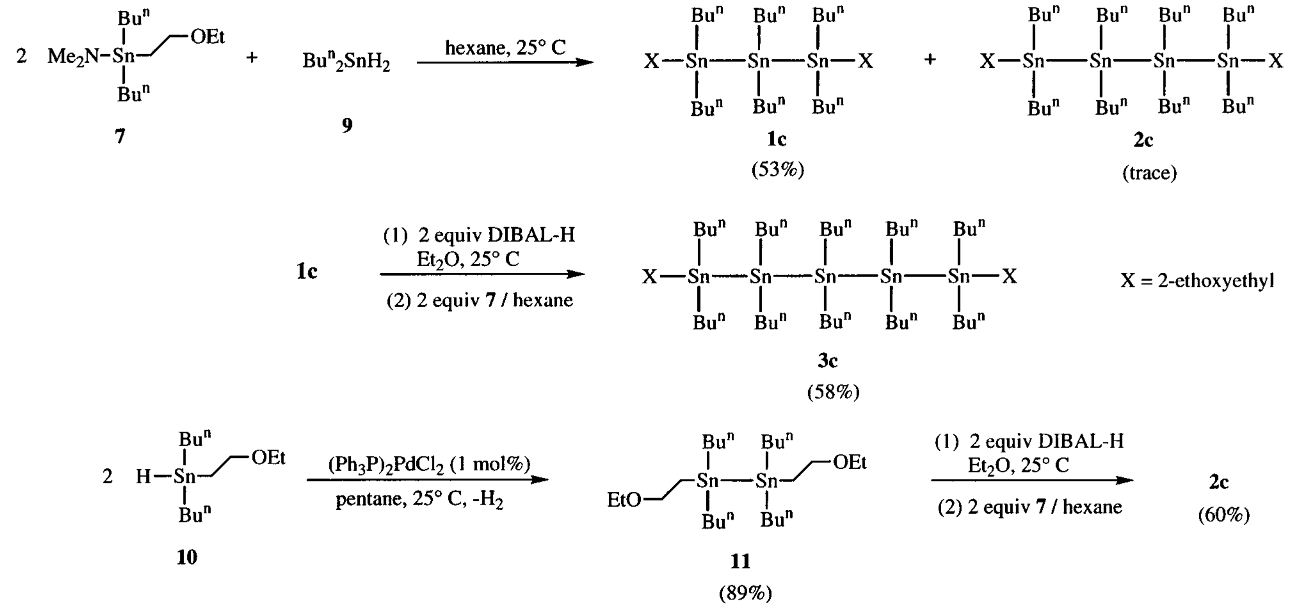


**Table 1. $\lambda_{max}$ (nm ($\epsilon_{max}$) for Oligostannanes 1−6**

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| **a** | 248 (30 100) (sh) | 274 (41 500) | 297 (54 700) | 312 (68 800) | 324 (84 000) | 342 (>66 000)[a] |
| **b** | 245 (22 377) (sh) | 270 (37 379) | 296 (46 040) | 310 (60 687) | | |
| **c** | 249 (31 000) (sh) | 273 (26 000) | 296 (49 700) | 312 | 323 | 340 |

[a] Due to the presence of a small amount of impurity, this $\epsilon_{max}$ represents a lower limit (see text).

**Table 2. Values of $^{119}$Sn Chemical Shifts (ppm) Recorded at 30 °C for the Indicated Oligostannanes[a,b]**

| | Sn$_1$ | Sn$_2$ | Sn$_3$ | Sn$_4$ | Sn$_5$ | Sn$_6$ |
|---|---|---|---|---|---|---|
| **1a** | −82.6 (Sn$_3$) | −86.9 | | | | |
| **1b** | −74.9 | −224.1 | −83.8 | | | |
| **1d** | −74.8 (Sn$_3$) | −81.3 | | | | |
| **2a** | −74.9 | −59.7 | −209.0 | −91.7 | | |
| **2b** | −74.4 | −212.2 | −210.5 | −82.5 | | |
| **2c** | −83.1 (Sn$_4$) | −210.4 (Sn$_3$) | | | | |
| **3a** | −91.1 (Sn$_5$) | −205.8 (Sn$_4$) | −35.8 | | | |
| **3b** | −74.0 | −208.3 | −197.8 | −206.6 | −82.4 | |
| **3c** | −83.0 (Sn$_5$) | −206.2 (Sn$_4$) | −197.1 | | | |
| **4a** | −79.6 | −205.9 | −33.5 | −194.0 | −207.8 | −85.2 |
| **5a** | −84.7 (Sn$_7$) | −206.5 (Sn$_6$) | −192.5 (Sn$_5$) | −27.7 | | |
| **6a** | −84.1 (Sn$_9$) | −204.4 (Sn$_8$) | −195.0 (Sn$_7$) | −189.3 (Sn$_6$) | −24.2 | |

[a] See Figure 1 for numbering of tin atoms. [b] Magnetically equivalent tin atoms are given in parentheses.

series **1a**−**6a** and **1c**−**6c**. Thus, from these data, it may be concluded that a single Bu$^n_2$Sn → Bu$^t_2$Sn replacement does not lead to any significant perturbation of the optical properties of oligostannanes as a result of either structural or electronic perturbations caused by the Bu$^t_2$Sn group.

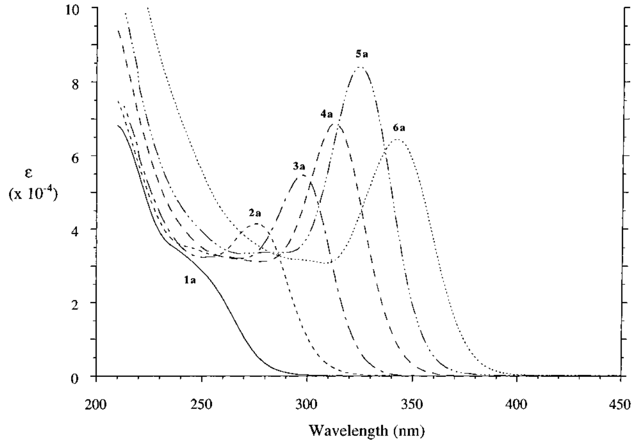


**Figure 2.** Electronic spectra for the oligostannanes **1a**−**6a**.

Given the favorable magnetic properties of tin,[7] $^{119}$Sn NMR spectroscopy provides an attractive tool by which to probe oligostannane electronic structure as nuclear magnetic properties are molecular electronic properties. For the present work, we were interested in determining whether perturbations in the values for $^{119}$Sn chemical shifts and $^1J(^{119}\mathrm{Sn}-^{119}\mathrm{Sn})$ could provide sensitive feedback for subtle changes that occur in the electronic properties of oligostannanes as a result of chain length and substituent effects. Table 2 and Figure 1 provide, respectively, values for $^{119}$Sn chemical shifts and $^1J(^{119}\mathrm{Sn}-^{119}\mathrm{Sn})$ that were obtained for the indicated oligostannanes, and Tables 3 and 4 provide values for longer range Sn−Sn coupling within the same set of compounds. Among the latter, which will not be discussed in any further detail, it is interesting to note that

**Table 3. Values of Geminal and Vicinal Couplings, $^{n}J(^{119}Sn-^{119}Sn)$ ($n$ = 2 and 3) (Hz), Recorded at 30 °C for the Indicated Oligostannanes[a,b]**

| | $^{2}J(Sn_1-Sn_3)$ | $^{2}J(Sn_2-Sn_4)$ | $^{2}J(Sn_3-Sn_5)$ | $^{2}J(Sn_4-Sn_6)$ | $^{3}J(Sn_1-Sn_4)$ | $^{3}J(Sn_2-Sn_5)$ | $^{3}J(Sn_3-Sn_6)$ |
|---|---|---|---|---|---|---|---|
| **1a** | 402 | | | | | | |
| **1b** | 463 | | | | | | |
| **1d** | 368 | | | | | | |
| **2a** | 259 | 182 | | | 217 | | |
| **2b** | 300 | 319 | | | 237 | | |
| **2c** | 322 | | | | 246 | | |
| **3a** | 153 | 118 | | | 213 | | |
| **3b** | 264 | 148 | 280 | | 222 | 222 | |
| **3c** | 288 | 140 | | | 266 | | |
| **4a** | 135 | 97 | 12 | 250 | 97 | 186 | 178 |
| **5a** | 244 | no[c] | 253 | | 175 | 182 | |

[a] See Figure 1 for numbering of tin atoms. Symmetry equivalent couplings are not shown. [b] $^{n}J(^{119}Sn-^{119}Sn)$ values were calculated from measurement of the observed $^{n}J(^{119}Sn-^{117}Sn)$ coupling constants. [c] Not observed, assumed to be <10 Hz.

**Table 4. Values of Long-range Coupling, $^{n}J(^{119}Sn-^{119}Sn)$ ($n$ > 3; Hz), Recorded at 30 °C for the Indicated Oligostannanes[a,b]**

| | $^{4}J(Sn_1-Sn_5)$ | $^{4}J(Sn_2-Sn_6)$ | $^{5}J(Sn_1-Sn_6)$ |
|---|---|---|---|
| **3a** | 67 | | |
| **3b** | 66 | | |
| **3c** | 65 | | |
| **4a** | 64 | 54 | 22 |
| **5a** | 54 | 60 | 19 |

[a] See Figure 1 for numbering of tin atoms. Symmetry equivalent couplings are not shown. [b] $^{n}J(^{119}Sn-^{119}Sn)$ was calculated from measurement of the observed $^{n}J(^{119}Sn-^{117}Sn)$ coupling constants.

even fairly long-range coupling constants, such as the value of 19 Hz for $^{5}J(^{119}Sn_1-^{119}Sn_6)$ in the heptastannane **5a**, which we believe to be the longest through-bond Sn−Sn coupling yet recorded for an oligostannane, can be resolved in the $^{119}Sn$ NMR spectra that routinely have a lower limit resolution of ca. 10 Hz.

From the complete $^{119}Sn$ NMR database for **1**−**6**, a few comments regarding chain length and substituent effects on $^{119}Sn$ chemical shift can be made. First, as previously observed, the chemical shift of a tin atom within an oligostannane is highly dependent upon both its location within the chain and the nature of its substituents, that is, more deshielded the further within the chain, $Bu^{t}_2Sn$ more deshielded than $Bu^{n}_2Sn$ (see Table 2).[4b,c,12] However, in contrast to the dramatic chain-length dependence of the $^{119}Sn$ chemical shift found by Adams and Dräger[4c] for the central $Bu^{t}_2Sn$ moieties in $Ph_3Sn-[Bu^{t}_2Sn]_n-SnPh_3$ ($n$ = 1−4), i.e., $\Delta\delta = (+50\ ppm)/n$, only an extremely small variance of this parameter occurs for the various tin atoms in **1**−**6**, with this variance dampening out rather quickly with chain length. We presume that this difference is related to the structural distortions occurring in the series of Adams and Dräger, and in this context, it is additionally important to note that, in the present work, a $Bu^{n}_2Sn \rightarrow Bu^{t}_2Sn$ substitution results in only a 0.5−1.5 ppm change in the chemical shifts of adjacent tin atoms. This observation further supports the view that this type of substitution does not produce significant steric interactions within the oligostannane that would lead to structural distortions.

In contrast to chemical shift, as Figure 1 reveals, the absolute magnitude of $^{1}J(^{119}Sn-^{119}Sn)$ for coupling between tin atoms in **1**−**6** is highly chain-length dependent. Within this trend, several important observations can be made. First, within the two $n$-butyl-substituted series **1b**−**4b** and **2c**, **3c**, there is a steady decrease in *all* $^{1}J(^{119}Sn-^{119}Sn)$ values as chain length increases. Were this to be simply the result of steric effects, one would perhaps not expect it to have such a dramatic influence on the terminal values as observed. Indeed, it is interesting to note that simple replacement of a $n$-butyl group by the 2-ethoxyethyl substituent has such a significant effect on $^{1}J(^{119}Sn-^{119}Sn)$. An alternative explanation then is that due to the phenomenon of $\sigma$-delocalization in linear group 14 polymetallanes,[1−4] as chain length increases, and the HOMO−LUMO gap of the oligostannanes decreases, increased negative contributions from excitations to higher molecular orbitals that are presumably $\sigma$-antibonding in character occur to reduce the magnitude of all $^{1}J(^{119}Sn-^{119}Sn)$ within a linear Sn−Sn-bonded backbone. More specifically, assuming the Fermi contact component to be dominant in determining the sign and magnitude of $^{1}J$, these negative contributions are to the mutual polarizability term, $\pi_{Sn-Sn}$ the magnitude of which depends on the relative energies of various electronic excited states.[10] A second, and curious, observation is that in the series **1a**−**6a**, the only clear pattern is that in going from **2a**, which has a remarkably small value of 27 Hz at 313 K, to longer chain lengths, there is a steady *increase* in the magnitude of the $^{1}J(^{119}Sn-^{119}Sn)$ values for Sn−Sn bonds made with a $Bu^{t}_2Sn$ atom. A possible solution to these puzzling observations might be found in comparing the values of $^{1}J(^{119}Sn-^{119}Sn)$ obtained for all the tri-, tetra-, and pentastannanes **1**−**3**. As noted previously, the electronic spectra for these compounds are virtually identical (see Table 1), however, it can be seen in every case that for the tri- and tetrastannanes, a $Bu^{n}_2Sn \rightarrow Bu^{t}_2Sn$ replacement produces a 600−750 Hz reduction in $^{1}J(^{119}Sn-^{119}Sn)$ for each Sn−Sn bond made with a $Bu^{t}_2Sn$ atom. If a similar reduction in magnitude occurs in going from **3c** to **3a**, this suggests that $^{1}J(^{119}Sn_2-^{119}Sn_3)$ in the latter pentastannane is actually negative in sign.[18] If steric effects can be ruled out as being responsible for the perturbation in $^{1}J(^{119}Sn-^{119}Sn)$ that is produced in performing a $Bu^{n}_2Sn \rightarrow$

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(16) Jousseaume, B.; Noiret, N.; Pereyre, M.; Saux, A. *Organometallics* **1994**, *13*, 1034−1038.

(17) Xi, R.; Babcock, J. R.; Sita, L. R. *Organometallics* **1996**, *15*, 2849−2851.

(18) A detailed analysis of rovibrational effects for the oligostannanes **1**−**6**, that are clearly observable by variable-temperature $^{119}Sn$ NMR, further supports the sign assignments of $^{1}J(^{119}Sn_2-^{119}Sn_3)$ and $^{1}J(^{119}Sn_3-^{119}Sn_4)$ in **3a** as being negative, as are the signs of each $^{1}J(^{119}Sn-^{119}Sn)$ in **2a** and **4a**−**6a** involving a $Bu^{t}_2Sn$ group, with the exception of $^{1}J(^{119}Sn_1-^{119}Sn_2)$ in **2a** that is positive in sign: Shibata, K.; Sita, L. R., submitted for publication.

$Bu^t{}_2Sn$ replacement in oligostannanes,[19] we are left with the conclusion that this substituent effect is electronic in nature. While the exact origin of this electronic effect of the *tert*-butyl group remains to be deduced, the results reported here suggest that such substituent effects may be important in governing the nuclear magnetic properties of heavy-atom systems to a greater extent than previously appreciated. Further, it is interesting to speculate that substituent electronic effects might also be behind the differences in chemical reactivity, and this could explain the pronounced behavior of the oligostannanes incorporating the $Bu^t{}_2Sn$ group to undergo *n*-butyl-group metathesis that is competitive with hydrostannolysis during the chain-length extension process. Additional studies are now in progress to further elucidate the origins, manifestations, and ramifications of substituent electronic effects in heavy-atom systems.

## Experimental Section

All manipulations were performed under an inert atmosphere using standard Schlenk and/or glovebox techniques. All solvents for synthesis were dried and distilled under nitrogen prior to use: tetrahydrofuran (THF) and diethyl ether ($Et_2O$) from sodium/benzophenone; toluene from sodium; hexane from lithium aluminum hydride ($LiAlH_4$). Silica gel (400 mesh, EM Scientific) for column chromatography was heated (300 °C) under vacuum for 3 days prior to use in the glovebox. Gravity chromatography was typically performed in a glovebox by using a 8 × 11 cm column of silica gel. Di-*n*-butyl(dimethylamino)(2-ethoxyethyl)stannane (**7**), di-*tert*-butylstannane (**8**), and di-*n*-butylstannane (**9**) were prepared according to previously reported procedures.[4d,20]

NMR spectra were recorded for $^1H$, $^{13}C$, and $^{119}Sn$ at 500, 75, and 186 MHz, respectively, using either benzene-$d_6$ or toluene-$d_8$ as the solvent. Tetramethyltin was used as the reference (0 ppm) for $^{119}Sn$ NMR spectra. UV spectra were recorded for pentane solutions. Chemical analyses were conducted by Oneida Research Services, Inc.

**1,1,3,3-Tetrabutyl-2,2-bis(1,1-dimethylethyl)-1,3-bis(2-ethoxyethyl)tristannane (1a).** A solution of 2.27 g (9.66 mmol) of **8** in 5 mL of hexane was added dropwise to 7.11 g (20.3 mmol) of neat **7** within a period of 8 min. The mixture was then stirred for 1 h at room temperature, whereupon the solvents were removed in vacuo to give an orange-colored crude material. This material was then filtered through a short pad of silica gel (4 × 3 cm), which was then rinsed with 150 mL of $Et_2O$, and the combined filtrates were concentrated in vacuo to give a light orange material. This crude product was then separated by column chromatography using a 70:1 hexane/$Et_2O$ solvent mixture as the eluant to provide 6.7 g (82%) of pure **1a**. For **1a**: $^1H$ NMR $\delta$ 0.99 (t, 12 H, $J = 7$ Hz), 1.17 (t, 6H, $J = 7$ Hz), 1.45 (s, 18 H), 1.2−1.8 (m, 28 H), 3.38 (q, 4 H, $J = 7$ Hz), 3.75 (t, 4 H, $J = 8$ Hz); $^{13}C\{^1H\}$ NMR $\delta$ 11.7, 13.1, 13.9, 15.7, 28.2, 29.7, 30.9, 34.5, 65.6, 70.2; $^{119}Sn\{^1H\}$ NMR, see text; UV see Table 1 and Figure 2. Anal. Calcd for $C_{32}H_{72}O_2Sn_3$: C, 45.48; H, 8.59. Found: C, 45.68, H, 8.82.

**1,1,2,2,4,4,5,5-Octabutyl-3,3-bis(1,1-dimethylethyl)-1,5-bis(2-ethoxyethyl)pentastannane (3a), 1,1,1,3,3,4,4-Heptabutyl-2,2-bis(1,1-dimethylethyl)-4-(2-ethoxyethyl)tetrastannane (2a), and 1,1,1,3,3,3-Hexabutyl-2,2-bis(1,1-dimethylethyl)-1,3-bis(2-ethoxyethyl)tristannane (1d).** To a solution of 900 mg (23.8 mmol) of $LiAlH_4$ in 40 mL of $Et_2O$, 2.68 g (11.9 mmol) of zinc bromide was added, and the mixture stirred at room temperature for 2 h. The mixture was then filtered through a pipet equipped with a plug of Kimwipe to provide a clear solution. This reagent was then added dropwise at room temperature to a solution of 6.5 g (7.69 mmol) of **1a** in 10 mL of hexane, and the mixture was stirred for 3 h. TLC analysis indicated the reaction to be incomplete, and so the process was repeated twice more until TLC showed that **1a** had been completely consumed. At this time, the solvents were removed in vacuo and 100 mL of hexane was added. The resulting suspension was then filtered through a pad of silica (4 × 2 cm), which was rinsed with 150 mL of hexane, and the combined filtrates were concentrated in vacuo to afford 5.44 g of a colorless liquid. This material was dissolved into 10 mL of hexane, and the solution was added dropwise to 5.38 g of neat **7**. The mixture was stirred at room temperature for 15 min, and then the solvents were removed in vacuo to give 10.48 g of a light yellow oil. This crude material was dissolved into 100 mL of $Et_2O$, and the solution was filtered through a pad of silica gel (4 × 3 cm), which was then rinsed with 150 mL of $Et_2O$, and the combined filtrates were concentrated in vacuo to give 7.8 g of a crude material. This was separated by column chromatography using a 40:1 hexane/$Et_2O$ solvent mixture as the eluant to provide 3.0 g (30% yield) of **3a** as a colorless oil. Two other fractions provided 3.48 g (30% yield) of **2a** and 390 mg (19% yield) of **1d**. For **3a**: $^1H$ NMR $\delta$ 1.00 (t, 12 H, $J = 7$ Hz), 1.02 (t, 12 H, $J = 7$ Hz), 1.18 (t, 6 H, $J = 7$ Hz), 1.50 (s, 18 H), 1.2−1.9 (m, 52 H), 3.39 (q, 4 H, $J = 7$ Hz), 3.76 (t, 4 H, $J = 7$ Hz); $^{13}C\{^1H\}$ NMR $\delta$ 10.9, 11.8, 13.3, 13.9, 13.93, 15.7, 28.1, 28.4, 30.2, 30.9, 33,52, 34.42, 65.7, 70.2; $^{119}Sn\{^1H\}$ NMR see text; UV see Table 1 and Figure 2. Anal. Calcd for $C_{48}H_{108}O_2Sn_5$: C, 43.98; H, 8.30. Found: C, 44.39; H, 8.61. For **2a**: $^1H$ NMR $\delta$ 0.9−1.8 (m, 72 H), 1.45 (s, 18 H), 3.38 (q, 2 H, $J = 7$ Hz), 3.73 (t, 2 H, $J = 7$ Hz); $^{13}C\{^1H\}$ NMR $\delta$ 10.64, 11.05, 11.72, 12.52, 13.19, 13.83, 13.87, 13.93, 15.66, 28.07, 28.15, 28.37, 29.88, 30.87, 30.91, 33.48, 34.47, 65.69, 70.19; $^{119}Sn\{^1H\}$ NMR see text; UV see Table 1 and Figure 2. Anal. Calcd for $C_{40}H_{90}OSn_4$: C, 45.24; H, 8.54. Found: C, 45.03; H, 8.47. For **1d**: $^1H$ NMR $\delta$ 0.9−1.8 (m, 72 H); $^{119}Sn\{^1H\}$ NMR see text; UV see Table 1. Anal. Calcd for $C_{32}H_{72}Sn_3$: C, 47.27; H, 8.93. Found: C, 48.01; H, 9.42.

**1,1,2,2,3,3,5,5,6,6,7,7-Dodecabutyl-4,4-bis(1,1-dimethylethyl)-1,7-bis(2-ethoxyethyl)heptastannane (5a) and 1,1,1,2,2,4,4,5,5,6,6-Undecabutyl-3,3-bis(1,1-dimethylethyl)-6-(2-ethoxyethyl)hexastannane (4a).** The same procedure used to prepare **3a** was used. Thus, addition of the reagent prepared from $LiAlH_4$ and zinc bromide was added dropwise to 3.03 g (2.31 mmol) of **3a** in 10 mL of hexane. This process was repeated until TLC showed that all of **3a** had been consumed. After separation from the insoluble material through the described process, 2.82 g of a light yellow oil was obtained, which was dissolved into 10 mL of hexane, and the solution was added dropwise to 2.20 g (5.78 mmol) of neat **7**. After the general workup and chromatography, 1.93 g (47% yield) of desired compound **5a** was obtained. Another fraction provided 0.43 g (4% yield) of **4a**. For **5a**: $^1H$ NMR $\delta$ 0.80−1.19 (m, 136 H), 3.38 (q, 4 H, $J = 7$ Hz), 3.71 (t, 4 H, $J = 7$ Hz); $^{119}Sn\{^1H\}$ NMR see text; UV see Table 1 and Figure 2. Anal. Calcd for $C_{64}H_{144}O_2Sn_7$: C, 43.26; H, 8.17. Found: C, 43.73; H, 8.52. For **4a**: $^1H$ NMR $\delta$ 0.80−1.19 (m, 122 H), 3.38 (q, 4 H, $J = 7$ Hz), 3.71 (t, 4 H, $J = 7$ Hz); $^{119}Sn\{^1H\}$ NMR see text; UV see Table 1 and Figure 2. Anal. Calcd for $C_{56}H_{126}OSn_6$: C, 44.02; H, 8.31. Found: C, 43.53; H, 8.55.

**1,1,2,2,3,3,4,4,6,6,7,7,8,8,9,9-Hexadecabutyl-5,5-bis(1,1-dimethylethyl)-1,9-bis(2-ethoxyethyl)nonastannane (6a).** Following the general procedure described for the synthesis of **3a** and **5a**, 1.13 g (638 $\mu$mol) of **5a** was first treated with the reagent prepared from $LiAlH_4$ and $ZnBr_2$ and then the

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(19) Given the long Sn−Sn bonds involved (cf., sterically unperturbed Sn−Sn bond lengths are in the range of 2.76−2.80 Å[10b]), it is also reasonable to assume that steric interactions between the *tert*-butyl and *n*-butyl substituents on adjacent tin atoms will be virtually nonexistent; a view that is additionally supported by molecular modeling and by the respective values of 2.798 Å and 106.9° reported for the Sn−Sn bond and Sn−Sn−Sn bond angle in the tristannane $Ph_3Sn{-}Bu^t{}_2Sn{-}SnPh_3$.[4c.]

(20) Neumann, W. P. *The Organic Chemistry of Tin*; Wiley: New York, 1970.

crude material from this reaction was added to 560 mg (1.60 mmol) of **7**. After the usual workup, 1.33 g of a light yellow oil was obtained, and this was subjected to fractionation by column chromatography, which provided 181 mg of the desired compound **6a** contaminated with a small amount of an inseparable impurity as revealed by $^{119}$Sn NMR. Although this impurity thwarted acquisition of a satisfactory chemical analysis, the identity of **6a** as the nonastannane was supported by both its $^{119}$Sn NMR and electronic spectra. For **6a**: $^1$H NMR $\delta$ 0.80−1.19 (m, 172 H), 3.38 (q, 4 H, $J = 7$ Hz), 3.71 (t, 4 H, $J = 7$ Hz); $^{119}$Sn{$^1$H} NMR see text; UV see Table 1 and Figure 2.

**1,1,2,2,3,3-Hexabutyl-1,3-bis(2-ethoxyethyl)tristannane (1c).** To a solution of 3.0 g (8.53 mmol) of **7** in 10 mL of hexane, a solution of 1.0 g (4.26 mmol) of **9** in 5 mL of hexane was slowly added dropwise. The mixture was stirred for 6 h, whereupon the solvents were removed in vacuo to provide 3.57 g of a light yellow oil. This crude material was subjected to column chromatography to provide 1.90 g (53% yield) of the desired compound **1c**. Another fraction provided 30 mg of pure **2c.** For **1c**: $^1$H NMR $\delta$ 0.80−1.19 (m, 64 H), 3.38 (q, 4 H, $J =$ 7 Hz), 3.71 (t, 4 H, $J = 7$ Hz); $^{13}$C{$^1$H} NMR $\delta$ 9.7, 12.0, 13.5, 14.5, 16.2, 28.6, 31.7, 32.5, 33.8, 66.2, 70.9; UV see Table 1. Anal. Calcd for $C_{32}H_{72}O_2Sn_3$: C, 43.98; H, 8.30. Found: C, 43.65; H, 8.20.

**1,1,2,2,3,3,4,4,5,5-Decabutyl-1,5-bis(2-ethoxyethyl)pentastannane (3c).** To a solution of 1.21 g (1.44 mmol) of **1c** in 5 mL of hexane, a solution of 512 mg (3.60 mmol) of diisobutylaluminum hydride (DIBAL-H) in 5 mL of hexane was slowly added dropwise of a period of 15 min. The mixture was stirred at room temperature for another 15 min and then filtered through a pad of silica gel (4 × 0.4 cm). The silica gel was washed with 250 mL of hexane, and then the combined filtrates were concentrated in vacuo to give 1.01 g of a colorless oil. This material was dissolved into 10 mL of hexane, and the solution was added dropwise to 1.1 g (3.17 mmol) of neat **7** over a period of 10 min. The mixture was stirred at room temperature for 20 min, and the solvents were removed in vacuo to give 2.03 g of a light yellow oil. The crude product was purified by column chromatography to provide 1.10 g (58% yield) of the desired product **3c**. For **3c**: $^1$H NMR $\delta$ 0.80−1.19 (m, 100 H), 3.40 (q, 4 H, $J = 7$ Hz), 3.75 (t, 4 H, $J = 7$ Hz); $^{13}$C{$^1$H} NMR $\delta$ 10.8, 11.5, 12.2, 13.7, 14.5, 16.2, 28.6, 28.8, 29.0, 31.7, 33.87, 33.93, 34.0, 66.2, 70.8; $^{119}$Sn{$^1$H} NMR see text; UV see Table 1. Anal. Calcd for $C_{48}H_{108}O_2Sn_5$: C, 43.98; H, 8.30. Found: C, 43.80; H, 7.83.

**1,2-Bis(2-ethoxyethyl)-1,1,2,2-tetrabutyldistannane (11).** To a solution of 2.32 g (7.56 mmol) of **10** in 20 mL pentane was added a suspension of 55 mg of dichlorobis(triphenylphosphine)palladium(II) in 5 mL of pentane, whereupon rapid gas evolution was observed immediately. The mixture was stirred for 2 h, after which time all gas evolution had ceased. The crude reaction mixture was filtered through a pad of Celite in a glass pipet equipped with a plug of Kimwipe, and the solvent was removed in vacuo to yield a pale yellow oil. This material was then bulb-to-bulb distilled (120 °C, $10^{-3}$ mmHg) to provide 2.06 g (3.36 mmol, 89%) of **11** as a colorless oil. For **11**: $^1$H NMR (benzene-$d_6$) $\delta$ 0.98 (t, 12 H, $J = 7.3$ Hz), 1.15−1.21 (m, 14 H), 1.44 (t, 8 H, $J = 7.3$ Hz), 1.50 (t, 4 H, $J = 7.5$ Hz), 1.69 (sext, 8 H, $J = 2.9$ Hz), 3.35 (q, 4 H, $J = 7.0$ Hz), 3.69 (t, 4 H, $J = 7.6$); $^{13}$C{$^1$H} NMR (benzene-$d_6$) $\delta$ 11.07, 12.67, 14.25, 15.93, 28.19, 31.30, 65.86, 70.45; $^{119}$Sn{$^1$H} NMR (benzene-$d_6$) $\delta$ −90 ($^1J(^{119}\mathrm{Sn}-^{117}\mathrm{Sn}) = 1407$). Anal. Calcd for $C_{24}H_{54}O_2Sn_2$: C, 47.09; H 8.89. Found: C, 47.14; H 8.95.

**1,1,2,2,3,3,4,4-Octabutyl-1,4-bis(2-ethoxyethyl)tetrastannane (2c).** To a solution of 1.5 g (2.45 mmol) of **11** in 5 mL of hexane, a solution of 700 mg (4.90 mmol) of diisobutylaluminum hydride (DIBAL-H) in 5 mL of hexane was slowly added dropwise over a period of 15 min. The mixture was stirred at room temperature for another 15 min and then filtered through a pad of silica gel (4 × 0.4 cm). The silica gel was washed with 250 mL of hexane, and then the combined filtrates were concentrated in vacuo to give 930 mg of a colorless oil. This material was dissolved into 10 mL of hexane, and the solution was added dropwise to 1.7 g (4.90 mmol) of neat **7** over a period of 10 min. The mixture was stirred at room temperature for 20 min, and the solvents were removed in vacuo to give 2.25 g of a light yellow oil. The crude product was purified by column chromatography to provide 1.58 g (60% yield) of the desired product **2c**. For **2c**: $^1$H NMR $\delta$ 0.80−1.19 (m, 82 H), 3.38 (q, 4 H, $J = 7$ Hz), 3.71 (t, 4 H, $J = 7$ Hz); $^{119}$Sn{$^1$H} NMR see text; UV see Table 1. Anal. Calcd for $C_{40}H_{90}O_2Sn_4$: C, 44.57; H 8.41. Found: C, 45.21; H 8.35.

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