Acc. Chem. Res. **1994,** *27,* 191–197

Heavy-Metal Organic Chemistry: Building with Tin

LAWRENCE R. SITA

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

Received February 14, 1994

After more than a century of research, synthetic methodology that can be used for the planned construction of molecular frameworks which incorporate the heavier group 14 elements (Si, Ge, Sn, and Pb) is still generally lacking. However, in recent years, strong motivation to remedy this situation is provided by growing evidence which suggests that, if obtainable, a large number of different structural classes for these heavy elements might be far more interesting to study than the organic compounds upon which they can be patterned. For instance, while linear polystannane oligomers of the general formula $R(SnR_2)_nR$ (R = alkyl or aryl) can formally be viewed as being heavy-atom structural analogs of *saturated* hydrocarbons, $H(CH_2)_nH$, an inspection of the electronic spectra for a homologous series of these compounds (e.g., $n = 3–6$) reveals that they more closely resemble *unsaturated* conjugated polyenes due to the occurrence of an intense low-energy absorption maximum which red-shifts with increasing chain length.[1] Similar behavior is observed for both polysilanes and polygermanes, and the current opinion is that this unique spectral feature originates with a "σ-delocalization" phenomenon that is an intrinsic property of the catenated chains of σ-bonded group 14 heavy atoms which represent the molecular backbones of these compounds.[2]

In order to place the concept of σ-delocalization for one of the more decidedly "metal-like" group 14 elements, tin, on a more solid theoretical foundation, and to possibly learn how to manipulate it to achieve a desired effect, we set out several years ago to devise new synthetic methodology that could be used to construct, by rational design, any molecular framework composed entirely of σ-bonded tin atoms (i.e., any polystannane). However, an initial review of the literature for target structures for which this methodology might be applied showed that, as of 1987, the known range of structural diversity for polystannanes was limited to only a few linear and cyclic structures, with no polycyclic polystannanes having ever been isolated and characterized.[1,3] This observation prompted us to wonder: if the unique properties of *linear* polystannanes are anything to go by, what marvels might be discovered with *polycyclic* polystannanes for which a far greater range of structural possibilities exist? To address this additional question, the objectives of the program were expanded to include a determination of what might be feasible within a three-dimensional architecture which utilizes tetracoordinate tetravalent tin atoms as the essential building block. This Account, then, is a summary of the progress that has been made to date toward the realization of these goals.

Lawrence R. Sita received his B.S. degree from Carnegie Mellon University in 1981. In 1985, he completed his Ph.D. degree at the Massachusetts Institute of Technology working with Professor Satoru Masamune and then remained at MIT, where he spent 1986 working with Professor Richard R. Schrock as a postdoctoral associate. In 1987, he returned to Carnegie Mellon University as an Assistant Professor of Chemistry, and in 1990 he moved his research program to the Beckman Institute in Pasadena, CA, where he held the position of Senior Research Fellow within the Division of Chemistry and Chemical Engineering at the California Institute of Technology. In 1994, he moved to his present position of Assistant Professor of Chemistry at The University of Chicago. His research interests include synthetic, structural, and mechanistic investigations of main group organometallic chemistry, transition metal mediated living polymerizations, and organized surfaces such as those found with self-assembled monolayers.

Polycyclic Polystannanes

A successful strategy used in the past to expand the range of known cyclic polystannane derivatives of the general formula $(R_2Sn)_n$ was to search for these compounds in product mixtures resulting from various oligomerization processes, and accordingly, it was felt that a similar strategy might be followed to quickly establish a new database of compounds that would include polycyclic polystannanes. To aid in the rapid selection of potential candidates from a large number of products, however, an additional strategy was adopted which consisted of focusing one's attention on only those compounds which are visibly colored (e.g., yellow to orange-red) since it could be rationalized that the absorptions responsible for this coloration arise from the σ-delocalization effects of an extended polystannane framework. As described more fully below, the incorporation of this strategy into the simple rule of thumb, "If it's colored, it's important", yielded a bonanza of results that firmly established that (1) a rich structural diversity apparently does exist for polycyclic polystannanes and (2) novel physical properties that are the consequence of unique molecular and electronic structures are indeed to be found for this class of compounds.

Bicyclo[2.2.0]hexastannanes. The reaction of organomagnesium halide and organolithium reagents with tin dichloride in ether solvents has a long history of producing highly-colored intractable materials, a partial analysis of which has revealed the presence of linear, branched, and cyclic polystannanes. Our interest in this reaction stemmed from the idea that, by employing 1-lithio-2,6-diethylbenzene (prepared *in situ* from the corresponding aryl bromide and *n*-butyllithium), the steric bulk of the 2,6-diethylphenyl substituent not only would limit the range of products that might be formed but also would aid in the "kinetic stabilization", and hence isolation, of any polystannane framework that was formed by providing a barrier that could shield

---

(1) Adams, S.; Dräger, M. *Angew. Chem., Int. Ed. Engl.* **1987,** *26,* 1255.

(2) (a) Miller, R. D.; Michl, J. *Chem. Rev.* **1989,** *89,* 1359. (b) Balaji, V.; Michl, J. *Polyhedron* **1991,** *10,* 1265.

(3) For representative cyclic polystannanes, $(R_2Sn)_n$, see, for $n = 3$: (a) Masamune, S.; Sita, L. R.; Williams, D. J. *J. Am. Chem. Soc.* **1983,** *105,* 630. For $n = 4$: (b) Puff, H.; Bach, C.; Schuh, W.; Zimmer, R. *J. Organomet. Chem.* **1986,** *312,* 313. For $n = 6$: (c) Dräger, M.; Mathiasch, B.; Ross, L.; Ross, M. *Z. Anorg. Allg. Chem.* **1983,** *506,* 99.

0001-4842/94/0127-0191$04.50/0

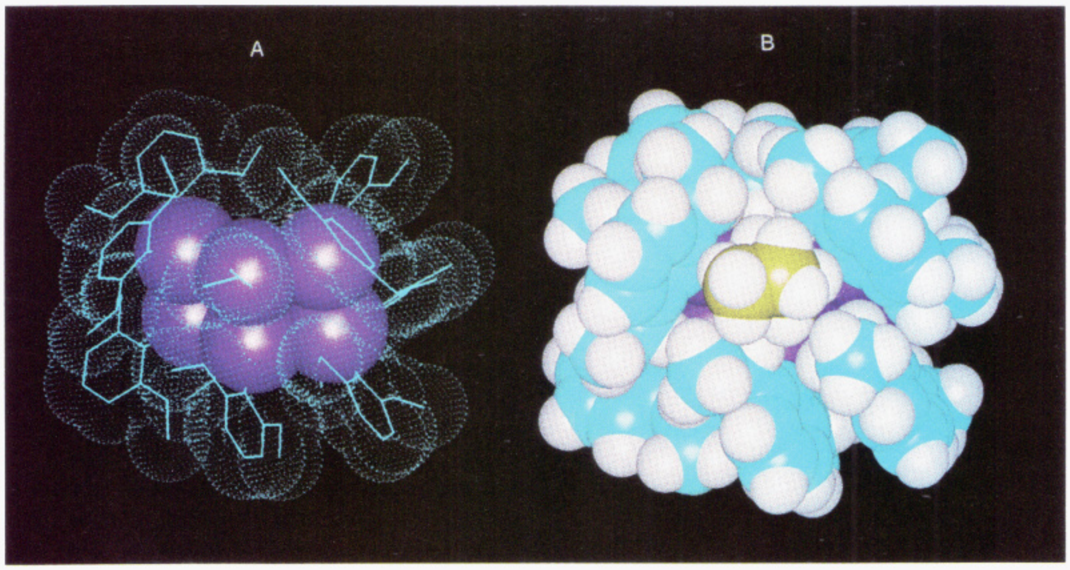
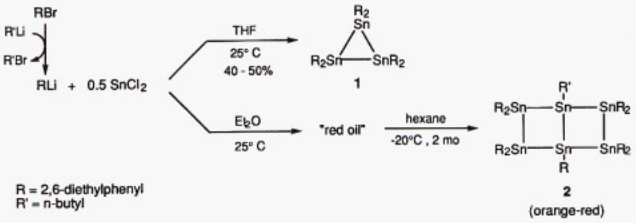


Figure 1. Space-filling representations of the molecular structure of compound **2**. (A) A view taken along the axis of the *n*-butyl substituent with the van der Waals surface of the carbon atoms being represented by a dotted pattern. Hydrogen atoms have been omitted for the sake of clarity. (B) The same view with all atoms being represented as CPK solid spheres.

Scheme 1



reactive tin–tin bonds from undesirable bimolecular reactions (e.g., oxygen atom insertion). As illustrated in Scheme 1, the composition of the product mixture obtained from this simple reaction proved to be highly dependent upon the nature of the solvent that was employed. For instance, with tetrahydrofuran, the reaction reproducibly provided a 40–50% yield of the previously known cyclotristannane derivative **1**[3a] as the sole polystannane product, whereas with diethyl ether, only a deep-red viscous oil was obtained. Perseverance at the fractional crystallization of this latter material, however, was finally rewarded by the appearance of beautiful orange-red single crystals which crystallographic analysis revealed to be the bicyclo[2.2.0]-hexastannane derivative **2**, possessing, for a set of substituents, one *n*-butyl and nine 2,6-diethylphenyl groups (Scheme 1).[4]

Due to a growing interest in the formulation of strain theories that can be used to assess the relative stability of various group 14 heavy atom analogs of organic structures, compound **2** represented an important benchmark that could be used to test the accuracy of recent theoretical predictions made by various researchers.[5] When a comparison between the experimentally determined structural parameters of **2** and those calculated by Nagase and co-workers[5] for the parent bicyclo[2.2.0]hexastannane system, **2a** (R = R′ = H in Scheme 1), was made, however, it became clear from the number of discrepancies that, as a result of small force constants for Sn–Sn bond length and Sn–Sn–Sn bond angle distortions, severe nonbonded interactions between organic substituents can conspire to shift the structural parameters of synthetic polycyclic polystannane derivatives well away from their preferred equilibrium values. Thus, for similar comparisons to work in the future, particular care must be exercised to select the steric bulk of a substituent on the basis of not only its ability to kinetically stabilize a specific polycyclic polystannane framework but also its ability to provide a derivative which will represent a good structural model for the parent compound. In this regard, an analysis of why the particular combination of substituents always appears in the formation of **2** is of interest since it might serve as the basis upon which future successful substituent/framework combinations can be derived through modeling. As Figure 1 shows, this analysis was performed by generating a space-filling representation of the molecular structure of **2** which clearly indicates that (1) the organic substituents serve to completely encapsulate the σ-bonded tin framework and (2) the nine 2,6-diethylphenyl groups work in concert to produce a cavity above one of the bridgehead tin atoms that can only accommodate the steric bulk of a *n*-butyl group rather than a tenth aryl substituent.

Concerning the relative stability of the bicyclo[2.2.0]-hexastannane system with respect to other polystannane structures known at the time, it was interesting to find that compound **2** survives intact in solution to temperatures of at least 200 °C, whereas the cyclotristannane **1** undergoes Sn–Sn bond disproportionation above 80 °C. This observation is consistent with the *ab initio* computational results of Nagase and co-workers,[5] who find that the parent bicyclo[2.2.0]-hexastannane (**2a**) is 13.2 kcal mol^{-1} more stable than the parent cyclotristannane (**1a**) (R = H in Scheme 1) as a result of a greater reluctancy of the heavier group 14 elements to engage in formal sp hybridization. As stated by these authors, this property tends to favor, in terms of strain energy, the formation of four-membered rings with 90° bond angles rather than three-membered rings with formal bond angles of 60°, thus further suggesting that four-membered rings might be

---

[4] Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 3769.
[5] Nagase, S. *Polyhedron* **1991**, *10*, 1299 and references cited therein.

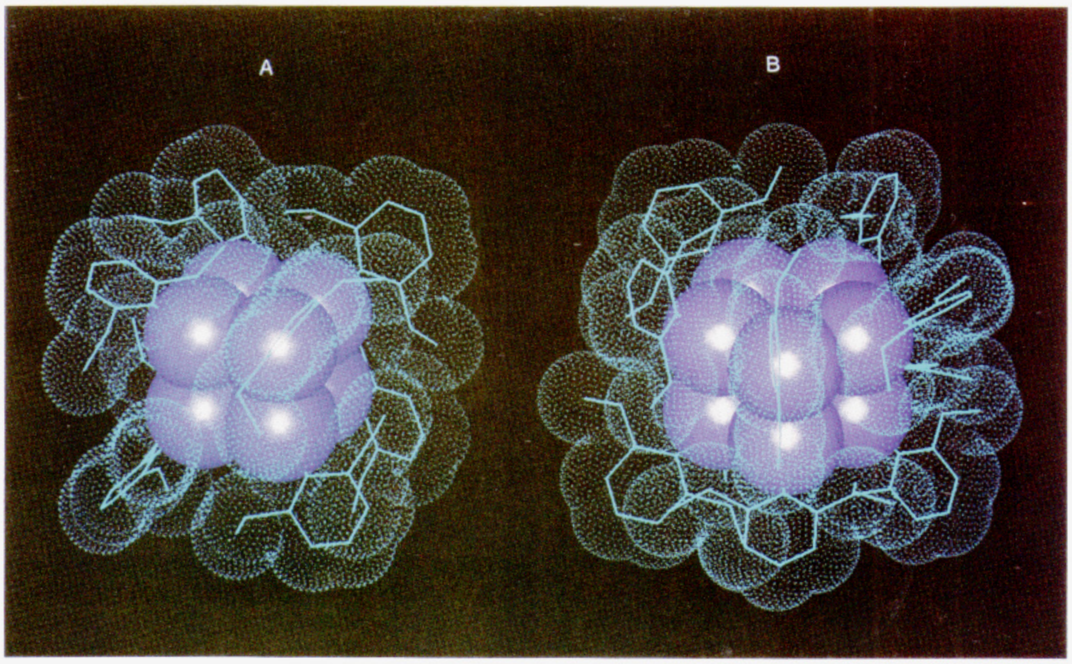
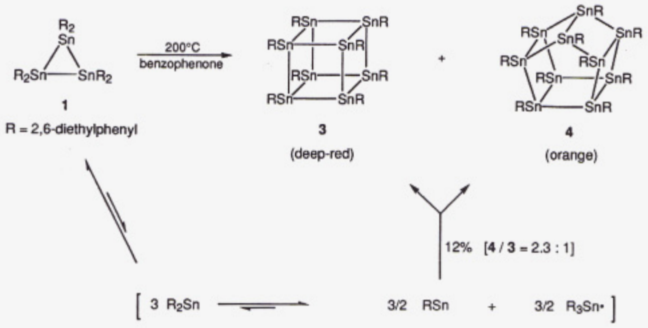


Figure 2. Space-filling representations of the molecular structures of (A) compound **3** and (B) compound **4**. The van der Waals surface of the carbon atoms is represented by a dotted pattern, and hydrogen atoms have been omitted for the sake of clarity.

a preferred structural motif of other stable (isolable) polycyclic polystannanes. In the absence of any data to the contrary, one could also view the calculated strain energy for the cyclotristannane ring system (i.e., 36.6 kcal mol^{-1} for **1a**) as potentially representing the upper limit on the amount of strain that can be accommodated by a polystannane framework. With this idea in mind, the search for other structures that might be formally more strained than **1a** commenced in earnest.

Perstanna[*n*]prismanes. As a precursor to oligomeric products, the cyclotristannane **1** was attractive since it begins to disproportionate in solution about 80 °C to the highly reactive monomeric stannylene species, R_2Sn. Perhaps not surprisingly, then, we found that, under more forcing conditions (e.g., 200 °C), a complex product mixture was generated which could subsequently be fractionated into a number of pure, highly-colored, air-sensitive tin-containing compounds by column chromatography on silica gel under an inert atmosphere. Fortunately, after considerable effort, these compounds could be induced to crystallize in almost every case and their structures could be unequivocally determined by crystallographic analysis. Once the existence of a particular compound was firmly established, the yield for its production could then be optimized by varying thermolysis conditions (e.g., solvent, temperature, time, etc.), and in this way, the new polycyclic polystannanes **3** and **4**, which are both representative members of the perstanna[*n*]prismane family of compounds possessing the general formula $[RSn]_{2n}$ (n = 4 and 5 for **3** and **4**, respectively), were discovered.[6,7] As Scheme 2 reveals, it was later found that **3** and **4** could best be produced by using benzophenone as the solvent, and this observation is rationalized on the basis that a higher concentration of the transiently generated stannylene, R_2Sn, might be achieved through solvent complexation which in turn leads, via bimolecular disproportionation, to a higher flux of the monovalent tin intermediate, RSn, that oligomerizes to produce the perstanna[*n*]prismanes.

Scheme 2

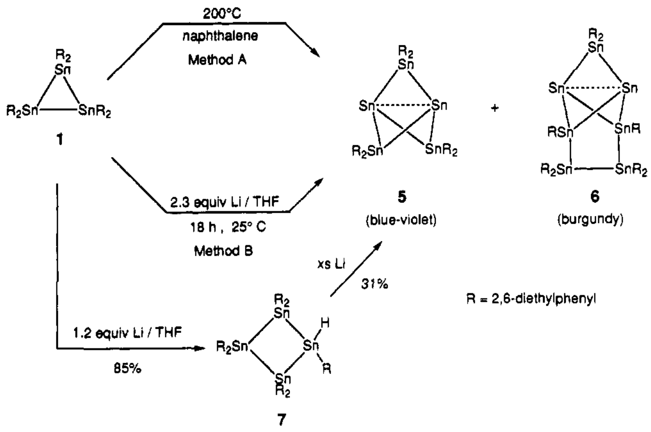


Both compounds **3** and **4** represent important compounds which can be used to test the reliability of theoretical predictions concerning group 14 heavy atom catenated structures, and for both of these perstanna[*n*]prismane derivatives, the 2,6-diethylphenyl group not only appears to be ideal for establishing an effective steric barrier that serves to completely encase their frameworks (see Figure 2) but also can do so without creating any severe nonbonded interactions between substituents that would cause undesirable strain-induced distortions to the frameworks. A very close correlation between the experimentally-derived structural parameters obtained for both **3** and **4** and those calculated for the parent system, **3a** (R = H in Scheme 2), or estimated from values calculated for the silicon analog of the parent system **4a** (R = H in Scheme 2) firmly establishes this latter feature of the 2,6-diethylphenyl group. Thus, from a structural point of view, compounds **3** and **4** appear to represent good model compounds for their respective parent perstanna[*n*]prismanes, and in the future, the information provided by the molecular structures of **3** and **4** should be important for identifying what other substituents might

(6) (a) Sita, L. R.; Kinoshita, I. *Organometallics* **1990**, *9*, 2865. (b) Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1991**, *113*, 1856.

(7) IUPAC nomenclature conventions for compounds **3** and **4** are pentacyclo[$4.2.0.0^{2,5}.0^{3,8}.0^{4,7}$]octastannane and hexacyclo[$5.3.0.0^{2,6}.0^{3,10}.0^{4,9}.0^{5,8}$]decastannane, respectively.

Scheme 3



be used to stabilize other derivatives of perstanna[*n*]prismanes for different values of *n* (i.e., *n* = 2, 3, or 6).

As a final note concerning perstanna[*n*]prismanes, it was important to discover that both **3** and **4** are photolytically and, at least to 200 °C, thermally robust, a property which is in sharp contrast to the relatively low thermal lability displayed by the cyclotristannane **1**. Since the parent compounds, **3a** and **4a**, are predicted to be *more strained* than the parent compound **1a** by 33.6 and 24.4 kcal mol^{-1}, respectively, these observations are important since they establish beyond a doubt that, as previously determined for organic structures, highly strained polycyclic polystannane frameworks can still be isolable if significantly high barriers toward disproportionation and rearrangement processes exist. Accordingly, it is clear that any discussion of the relative stability of a group 14 heavy atom catenated structure must include both an evaluation of the depth of the minimum which represents that structure and an evaluation of the potential energy surface in the vicinity of that minimum.

Perstanna[1.1.1]propellanes. Of the other highly-colored compounds that could be obtained from thermolysis of the cyclotristannane **1**, two were of immediate interest to us due to the quite distinctive colors of their solutions, which are *blue-violet* and *burgundy*; and as Scheme 3 shows, crystallographic analysis revealed them to be the two perstanna[1.1.1]propellane derivatives **5** and **6**, respectively.[8,9] Putting aside for a moment the obvious questions concerning the mechanism of their formation and the nature of bonding in these frameworks, it is interesting to point out that, once the identities of **5** and **6** were known, these two compounds, surprisingly, could be found, from trace to significant amounts, in a number of product mixtures that were obtained from various sources, the most interesting of these involving reduction of the cyclotristannane **1** with lithium metal at room temperature (method B in Scheme 3).[8b] Since this reaction, which has been determined to proceed through initial formation of the cyclotetrastannane derivative **7** (Scheme 3), produces few side products and reproducibly provides **5** in modest yields (31%), it is the procedure of choice for obtaining significant amounts of the two perstanna[1.1.1]propellane derivatives.

In the absence of air, both perstanna[1.1.1]propellanes **5** and **6** appear to be indefinitely stable, and given their intriguing structural geometries, one question that *immediately comes to mind* is, why? As a start of an answer to this question, the space-filling representation of the molecular structure of **5** shown in Figure 3 provides important clues concerning how the 2,6-diethylphenyl substituent can kinetically stabilize this particular polycyclic polystannane framework. Thus, a side view (Figure 3A) shows that the five tin atoms of **5** are completely encapsulated, whereas a front view (Figure 3B) reveals how each of the two bridgehead tin atoms resides at the bottom of a molecular cavity that has been formed by the cooperative interaction of six ethyl groups on each side of the molecule. Using this latter view, it can be further determined that the cavity is fairly small (*ca.* 4 Å in diameter), and this undoubtedly helps to prevent close interactions due to self-association from occurring and, thereby, retard the polymerization process which is known to spontaneously occur for the carbon [1.1.1]propellane analog, C_5H_6, in concentrated form.[10]

Central to the question of stability of **5** and **6** is the issue of the nature of bonding between the two bridgehead tin atoms in these structures which are *forced to adopt inverted tetrahedral geometries if they* are considered to be tetracoordinate. Interestingly, prior to our isolation and characterization of **5**, the identical question concerning the nature of bonding in the parent pentasila[1.1.1]propellane, Si_5H_6, was being considered by several different theoretical groups, and their conclusion was that if any formal bond existed between the two bridgehead silicon atoms in this structure, then it must be extremely weak.[11] Experimentally, the values for the distance between the two bridgehead tin atoms in **5** and **6** were determined to be 3.367(1) and 3.348(1) Å, respectively, which, when compared to the value of 3.361(1) Å determined for the nonbonding distance between the two bridgehead tin atoms in a bicyclo[1.1.1]pentastannane derivative,[12] seem to support the nonbonding or extremely weak bonding picture described above. Further support for this is provided by Gordon and co-workers,[13] who recently calculated a corresponding distance of 3.463 Å for the parent pentastanna[1.1.1]propellane system, **5a** (R = H in Scheme 3), and determined, through Bader analysis, that no bond critical point, which would represent a formal bond path, appears in the inter-bridgehead region of **5a** as it does in the case of the carbon [1.1.1]propellane analog.[14] Finally, on the basis of the qualitative molecular orbital diagram that was beginning to emerge, it was rationalized that the products resulting from one- and two-electron reduction of perstanna[1.1.1]propellanes should be stable species since the lowest occupied molecular orbital (LUMO) that is being filled upon reduction is essentially the

---

[8] (a) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 6454. (b) Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1992**, *114*, 7024.

[9] IUPAC nomenclature conventions for compounds **5** and **6** are tricyclo[1.1.1.0^{1,3}]pentastannane and tetracyclo[4.1.0.0^{1,5}.0^{2,6}]heptastannane, respectively.

[10] Wiberg, K. B. *Chem. Rev.* **1989**, *89*, 975 and references cited therein.

[11] (a) Schleyer, P. v. R.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1267. (b) Nagase, S.; Kudo, T. *Organometallics* **1987**, *6*, 2456. (c) Schoeller, W. W.; Dabisch, T.; Busch, T. *Inorg. Chem.* **1987**, *26*, 4383. (Also see: Kitchen, D. B.; Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1990**, *112*, 3408.)

[12] Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1990**, *112*, 8839.

[13] Gordon, M. S.; Nguyen, K. A.; Carroll, M. T. *Polyhedron* **1991**, *10*, 1247.

[14] For a discussion of bond critical points and bond paths as they relate to molecular structure, see: (a) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9. (b) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985.

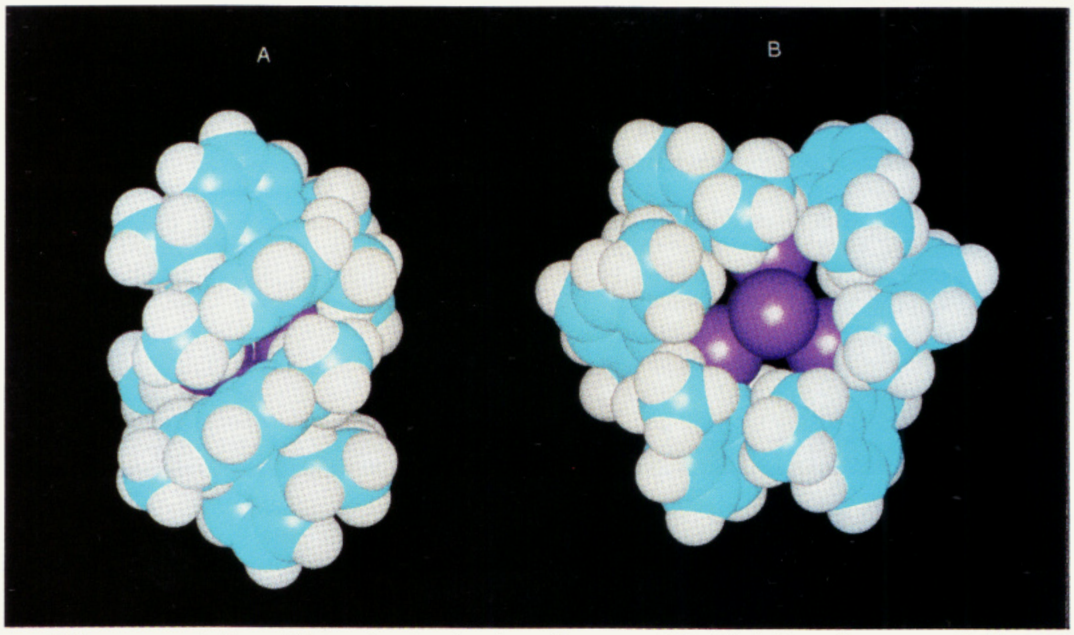
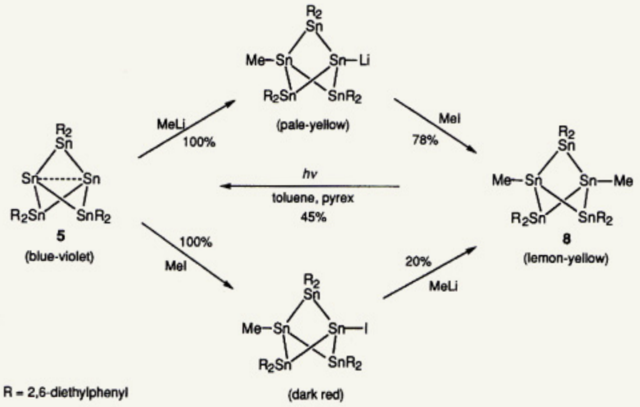


Figure 3. Space-filling representations of the molecular structure of compound **5**. (A) A view taken prepedicular to a plane defined by the two bridgehead tin atoms and one bridging tin atom. (B) A view taken perpendicular to the plane defined by all three bridging tin atoms. All atoms are represented as CPK solid spheres.

antisymmetric form of the highest occupied molecular orbital (HOMO), which correlates with the interaction between the two bridgehead tin atoms that is predominantly nonbonding in character. This idea was borne out by cyclic voltammetry studies which confirm that both **5** and **6** undergo two reversible one-electron reductions, and by chemical reduction experiments that provided the stable radical anion species, $[\mathbf{5}]^-$ and $[\mathbf{6}]^-$, which were fully characterized by electron spin resonance (ESR) spectroscopy; a method which reveals that spin density is delocalized within the frameworks of these compounds over five and seven tin atoms, respectively.[8b,12] In conclusion then, a majority of experimental and theoretical studies appear to agree that, for perstanna[1.1.1]propellanes, a bond between the two bridgehead tin atoms is virtually nonexistent. However, since some structure/property relationships derived from a comparison between **5** and **6** tend to suggest to the contrary that a significant bonding interaction may be present,[8b] it is likely that the question of bonding in perstanna[1.1.1]propellanes will not be definitively settled until additional synthetic derivatives are isolated and these structure/property relationships more firmly established.

Bicyclo[1.1.1]pentastannanes. Until now, little has been said of the chemical reactivity of the polycyclic polystannanes that have been mentioned above; however, it can be appreciated that, in the future, these compounds may serve as important starting materials for the synthesis of a variety of new structural classes. In fact, for perstanna[1.1.1]propellanes, this expectation has already been realized by the demonstration that the derivative **5** can be used to produce bicyclo[1.1.1]pentastannanes by the reactions shown in Scheme 4.[15] The success of the addition reactions involving **5** results from the utilization of reagents that are small enough to insert into the cavity formed by the 2,6-diethylphenyl groups (see Figure 3B), and this appears to be limited to substituents with a steric demand similar to that of a methyl group. Even in this case, however, the significant increase in nonbonded interactions that occur upon the addition of these bridgehead methyl substituents leads to a substantial increase in the overall strain of the bicyclo[1.1.1]pentastannane system which, in turn, manifests itself as anomalous chemical and spectroscopic behavior for all of the derivatives that have been prepared to date. For instance, photolysis of compound **8** produces the pentastanna[1.1.1]propellane **5** again in a 45% yield (Scheme 4). In addition, the magnitude of the one-bond nuclear spin–spin coupling constant, $^1J(^{119}\mathrm{Sn}_{\mathrm{br}}-^{119}\mathrm{Sn}_{\mathrm{bh}})$ (br = bridging; bh = bridgehead), for this derivative was found to be dramatically temperature dependent by ^{119}Sn NMR spectroscopy.[15] Once more, due to the small force constants associated with deformations of polycyclic polystannane structures, this unprecedented behavior for a stereochemically rigid molecule can be seen as arising from the facilitation of framework deformations, such as a "breathing" mode expansion, at higher temperatures by an increase in nonbonded interactions between substituents brought about by an increase in torsional mobility.

Scheme 4



---

[15] Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1991**, *113*, 5070.

Rational Synthesis of Polystannane Frameworks

The ability to obtain a fairly large number of structurally unique polycyclic polystannanes in such a relatively short period of time, together with a documentation of their thermal stability, suggested to us that the full range of structural diversity for these compounds could easily begin to rival that of organic molecules *if* procedures that can be used for their construction via rational design could be developed. From a synthetic chemist's point of view, this objective was translated into the need to establish (1) a facile and directional method for the construction of Sn–Sn bonds, (2) a set of orthogonal protecting groups that can be selectively and quantitatively removed to reveal new sites for framework extension, and (3) new methods of purification and analysis to ascertain that the polystannane products are homogeneously and homologously pure. As discussed more fully below, these requirements have now been met for the simple polystannane structural classes.

Linear Polystannanes. Our approach to the construction of polystannane frameworks was to adopt the hydrostannolysis reaction for the critical Sn–Sn bond-forming procedure since it has previously been used successfully for high-yielding syntheses of linear tri- and tetrastannanes according to reaction 1.[16]

$$H(R_2Sn)_nH + 2R'_3SnNMe_2 \underset{n=1 \text{ or } 2}{\longrightarrow} R'_3Sn(R_2Sn)_nSnR'_3 + 2HNMe_2 \quad (1)$$

However, in order to apply this synthetic methodology for the intended purpose, a protecting group was required that could be removed, after hydrostannolysis, to reveal a new functionality that could then serve as the site for extension of the polystannane backbone. After several different methods were explored, it was decided that the β-alkoxy substituent might be able to function in this capacity by being susceptible to reagents that are typically employed to remove the 2-(trimethylsilyl)ethyl ether ($Me_3SiCH_2CH_2OR$) protecting group that is used in organic synthesis.[17] Indeed, as Scheme 5 indicates, this strategy worked exceedingly well. Thus, several reagents with the general formula of **9** could easily be prepared through hydrostannation of vinyl ethyl ether with different chloro diorganostannanes, RR″SnHCl (reagent synthesis, Scheme 5).[18] In addition, it was found that the β-ethoxyethyl substituent could be quantitatively removed in a variety of ways to generate new tin-centered functional groups that are suitable for use in subsequent hydrostannolysis reactions (deprotection, Scheme 5). For example, by employing diisobutylaluminum hydride (DIBAL-H), a tin hydride moiety (i.e., Sn–H) can be produced, whereas, with zinc dibromide or iodotrimethylsilane, the β-ethoxyethyl group is transformed into Sn–Br and Sn–I functional groups, respectively. Since these latter two groups can be further converted to tin amides (e.g., R_3SnNMe_2), it is evident that convergent syntheses of polystannane frameworks via the coupling of two fragments that arise from a common precursor should be possible by utilizing the synthetic methodology shown in Scheme 5.

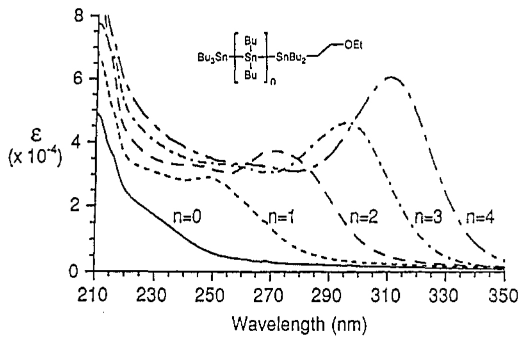
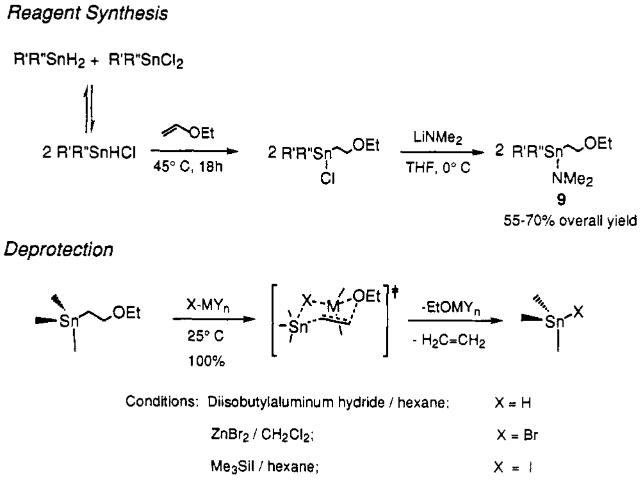
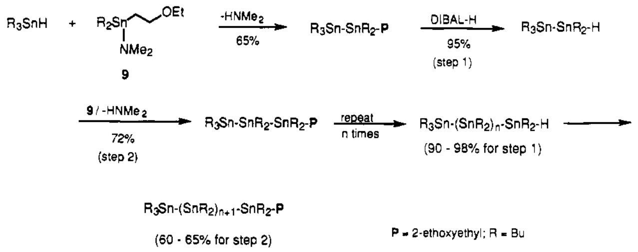


Figure 4. A comparison of the electronic spectra for a homologous series of linear polystannanes prepared according to Scheme 6. Reprinted with permission from ref 18. Copyright 1992 American Chemical Society.

Scheme 5



Scheme 6



As Scheme 6 shows, the reagents and transformations described above were utilized for the stepwise construction of a homologous series of linear polystannane oligomers, the electronic spectra of which are compared in Figure 4.[18] It is of perhaps primary importance that this synthetic strategy allows one to purify each intermediate to homogeneity by conventional column chromatography. To ascertain that the polystannane products are homologously pure, several analytical methods are employed, and these include both reverse-phase high-pressure liquid chromatography (HPLC) and ^{119}Sn NMR spectroscopy. Interestingly, this latter method unexpectedly revealed, for the series of linear polystannanes shown in Figure 4, anomalous temperature-dependent behavior of all of the spin–spin coupling constants, ^nJ, including those involved in coupling

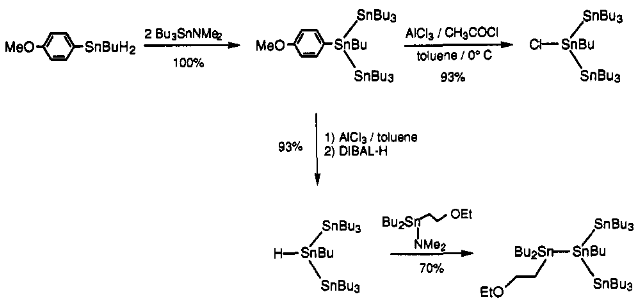
---

(16) (a) Sommer, R.; Schneider, B.; Neumann, W. P. *Justus Liebigs Ann. Chem.* **1966**, *692*, 12. (b) Neumann, W. P. *The Organic Chemistry of Tin*; Wiley: New York, 1970. (c) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, U.K., 1980.

(17) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley Interscience: New York, 1991.

(18) Sita, L. R. *Organometallics* **1992**, *11*, 1442.

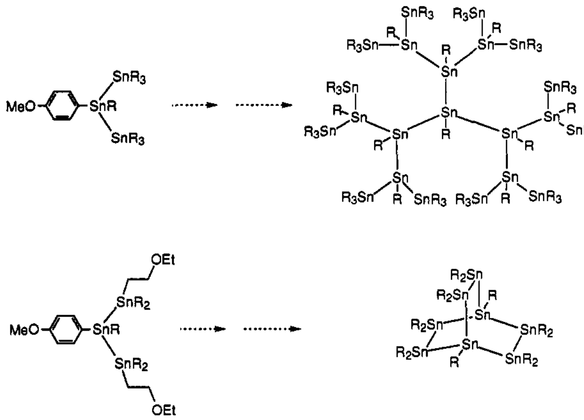
Scheme 7



through only a single bond.[19] In addition, a unique inverse relationship between chain length and the absolute magnitudes of all of the ^nJ values are observed. Clearly further studies are still required to elucidate more precisely the structure/property relationships that govern the physical properties of linear polystannanes, and to this end, the synthetic methodology given in Schemes 5 and 6 should allow one to systematically probe the impact that chain length and the nature of the substituents have on the molecular and electronic structure of these materials.

Branched Polystannanes. In order to be able to assemble more complex polystannane structures, it is necessary to have a set of orthogonal protecting groups; that is, one protecting group can be selectively removed in the presence of the other. It is also necessary to be able to generate new Sn–H and Sn–Cl functional groups at internal positions of the polystannane framework so that branch points can be incorporated into the structure. Fortunately, both of these conditions can be met through the use of the *p*-methoxyphenyl substituent as a protecting group, which, as Scheme 7 reveals, has been used for the controlled construction of isomeric branched polystannanes.[20] Key to the success of this reaction scheme was the identification of conditions that would remove the *p*-methoxyphenyl group and leave Sn–Sn bonds intact. While this proved to be a challenging task, the two methods that are shown were eventually found that could directly produce either Sn–H or Sn–Cl functional groups, thus, further promising the prospect of future convergent syntheses of symmetric complex polystannanes from common precursors. More importantly, the *p*-methoxyphenyl group is not affected by the conditions which are used to remove the β-ethoxyethyl substituent, thereby establishing the orthogonality of these two protecting groups.

Scheme 8



Concluding Remarks

Although far from being complete, the research described in this Account has unequivocally established several important points: (1) a rich structural diversity for σ-bonded polystannane frameworks does exist; (2) highly strained polycyclic polystannanes can be quite stable by virtue of substantial barriers to rearrangements or bond dissociations; and (3) the concepts and strategies of organic chemistry can be successfully applied to the development of new synthetic methodology that is useful for the construction of polystannane frameworks via rational routes. Having laid this foundation then, it is not difficult to imagine what may now be possible in the near future. For instance, it should be feasible, by employing the tools that are already at hand, to construct the new classes of compounds shown in Scheme 8, which, as based on our previous experience, should possess novel properties. With these thoughts, it also becomes clear that, concerning polystannanes, we need no longer wonder what might be possible, but rather, we can now focus on the more exciting task of proving what is *not* possible.

This research was supported by the National Science Foundation, the Office of Naval Research, and the Petroleum Research Fund, for which I am grateful. I am also indebted to my talented co-workers who solved a number of difficult synthetic and technical problems that brought the research to fruition: Richard D. Bickerstaff, Isamu Kinoshita, and Karl W. Terry.

---

(19) Sita, L. R. Unpublished results.
(20) Terry, K. W.; Sita, L. R. Unpublished results.