

CHEMISTRY A European Journal



Accepted Article Title: Synthesis and Characterization of Readily Modified Poly(aryl) (alkoxy)stannanes by use of Hypercoordinate Sn Monomers Authors: Jeffrey A Pau, Gloria M D'Amaral, R. Stephen A Wylie, Alan J Lough, and Daniel Alain Foucher This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article. To be cited as: Chem. Eur. J. 10.1002/chem.201804145 Link to VoR: http://dx.doi.org/10.1002/chem.201804145

Supported by ACES



DOI: 10.1002/marc.((insert number)) ((or ppap., mabi., macp., mame., mren., mats.))

Article

Synthesis and Characterization of Readily Modified Poly(aryl)(alkoxy)stannanes by use of Hypercoordinate Sn Monomers

Jeffrey Pau, Gloria M. D'Amaral, Alan J. Lought, R. Stephen Wylie, and Daniel A. Foucher *

J. Pau, G. M. D'Amaral, Prof. R. S. Wylie, Prof. D. A. Foucher Advanced Materials Laboratory, Department of Chemistry and Biology, Ryerson University 350 Victoria Street, Toronto, ON, Canada, M5B 2K3 E-mail: daniel.foucher@ryerson.ca Dr. A. J. Lough X-ray Laboratory Department of Chemistry University of Toronto, Toronto, ON, Canada M5H 3H6

The synthesis and solid-state molecular structures of two dichlorido(aryl)(alkyl) tin compounds, **5** and **8**, both key intermediates to tunable polystannane architectures, is reported. The materials are further investigated by single-crystal XRD and a DFT analysis of their preferential "open and closed" geometries. Conversion of said compounds to their dihydride analogues was undertaken followed by their application as monomers for polystannane polymer synthesis. The properties of two asymmetrical polystannanes thus prepared by transition metal-catalyzed dehydropolymerization of dihydrido(aryl)alkylstannanes (**6** and **9**) were investigated. The first is the structurally simple, modest molecular weight, semi-crystalline light and moisture stable polystannane (**10**) with NMR (¹¹⁹Sn) evidence of prominent Sn \leftarrow O hypercoordination along the polymer backbone. The second is a lower molecular weight, functionally tosylated four coordinate polystannane (**11**) with no evidence of hypercoordination. Thermal analysis (DSC) of polymer **10** reveal a reversible semi-crystalline nature, while only amorphous behavior was detected for polymer **11**. Polystannane **10** was also found to be exceptionally stable to both

moisture and light (> 6 months) and a promising candidate for the design of readily modified (i.e. tunable) polystannane materials.



Chemistry - A European Journal

1. Introduction

Dialkyl or diaryl linear polystannanes are main group polymers constructed of a backbone of covalently bound tin atoms.^[1-3] There are a multitude of ways to prepare polystannanes. The first well characterized examples were reported by Tilley and co-workers in 1993 and were prepared by dehydrogenative coupling of diorganostannanes in the presence of an early transition metal catalyst.^[4-6] More recently, Caseri *et al.* have demonstrated the successful dehydrocoupling of dialkylstannanes to yield cyclic-free high molecular weight (10^5 Da) polystannanes, such as 1, in the presence of a late transition metal complex (i.e. Wilkinson's Catalyst).^[7,8] This Rh compound was identifed by Caseri and coworkers as the most efficient dehydropolymerization catalyst for dialkyltin dihydrides from the testing of over thirty transition metal complexes.^[7,9] Earlier work by Molloy *et al.* had also shown that high molecular weight (10^5 Da) polystannanes can be prepared via a low-temperature ($60 \, ^\circ C$) Namediated Wurtz coupling of dialkyltin dichlorides^[10] or alkylaryltin dibromides^[11] in toluene in the presence of 15-crown-5. Lower molecular weight (10^3 Da) polystannanes were more recently obtained by Caseri and coworkers from the Wurtz coupling of dialkyltin dichlorides in liquid ammonia.^[8,12] Electrochemical coupling of dialkyltin dichlorides to low molecular weight polymers (10^3 Da) has also been demonstrated by Okano and coworkers.^[13,14] In 2015, Harrypersad and Foucher described the preparation of moderate molecular weight $(10^4 - 10^5 \text{ Da})$ alternating polystannanes from the condensation polymerization of diaryl or dialkyl tin dihydrides with appropriately chosen dialkyltin diamides.^[15]

This article is protected by copyright. All rights reserved.



Figure 1: Relative solution stability of different polystannane backbones to visible light.^[5,16,17]

Characteristic of polystannanes is their unusual electronic properties which are derived from the σ - σ overlap of diffuse formally $5sp^3$ hybridised tin orbitals that translate into a detectable visible absorption in the 390-450 nm range. Unfortunately, these intriguing low band gap intrinsic semi-conducting materials (2-4 eV) suffer from acute sensitivity to both light and moisture. The origins of this sensitivity has been correlated to the presence of long, weak Sn-Sn bonds of the Lewis acidic tin centres along the polymer backbone that are susceptible to radical cleavage and nucleophilic attack. Extensive efforts by Caseri and co-workers have shown that light induced degradation of polystannanes proceeds by an "unzipping" mechanism. The addition of light stabilizers that absorb in the visible range can dramatically increase the stablity of dialkylstannanes.^[18,19] Diaryl containing polystannanes also show inherently improved stability in comparison to the dialkyl analogues, likely due to the increased $\sigma - \pi$ mixing of the ligand orbitals when directly bound^[20] to tin, or as a light absorbing moiety incorporated into the Sn containing skeleton.^[21] One exception to this is the extreme light sensitivity observed for polystannanes bearing strong electron-withdrawing substituents, such as any groups containing CF_3 functionalities (2), which presumably increase the Lewis acidic nature of tin.^[22] In addition to the pronounced sensitivity to light of these polystannanes, poor

- 4 -

10.1002/chem.201804145

stability to ambient moisture also leads to the formation of stannoxane degradation products likely via nucleophilic attack by H₂O on the Sn atoms.^[5]

A new approach to address the light and moisture stability concerns of polystannanes was recently investigated by Foucher *et al.* who proposed the use of hypercoordinate architectures at tin centers to provide both an electronic and steric solution to address these stability issues.^[17] The use of light absorbing azo-containing propyloxy substituents on the metal centers revealed strong hypercoordination in small molecule species, with evidence of two well separated distinct tin signals in the ¹¹⁹Sn NMR of the polystannane **3** (Figure 1) assigned to both open and closed configurations within the polymer. This homopolymer proved to be indefinitely stable to ambient conditions for > 2 years and is the first example of a truly stable polystannane.

To understand the "design rules" for constructing stable polystannanes more broadly, the role of the ligand in hypercoordination must be understood. Synergistic push-pull interactions, such as those defined by 3-center-4-electron hypercoordination arrangements have been known for at least 50 years between the later Group 14 elements (Si, Ge, Sn, Pb), electron rich N, P, O and S donor atoms and axially coordinated electron-withdrawing substituents (CI⁻, Br⁻, I⁻).^[23,24] X-ray structural data for several of these Sn species reveals additional donor ligand coordination to the Group 14 element along with an elongation of the ligand-metal bond *trans* to the donating group.^[25–32] Hypercoordination to a Sn center is theorized to be the result of a 2e donation from the formal p-orbital of the donating ligand into an empty non-bonding orbital of Sn, which then simultaneously transfers electron density on to an antibonding p-orbital of the electron-withdrawing substituent.^[33] Facile hypercoordination in these species is likely a result of the high formal oxidation state at Sn and hence pronounced Lewis acidic character of the Sn(IV) center. The role of the Sn atom in such 3c-4e interactions for the most part is unknown, but it appears to function as an efficient electron shuttle. If the electron withdrawing substituent(s) are replaced with one or two equally deficient electron Sn atom(s), such as those

present in hypercoordinated polystannanes, the opportunity to deploy additional electron density to the Sn backbone could result in stronger Sn-Sn bonds. This would, in turn, possibly make the metal-metal bonds less susceptible to undergo cleavage in the presence of nucleophiles such as H_2O .^[5,34,35]

Herein, we describe the preparation of a semi-crystalline, moderate molecular weight hypercoordinated polystannane (*i.e.*, **10**). This asymmetrical polystannane also possesses exceptional light and moisture stability over several months of exposure to ambient atmosphere, with no observed changes in molecular weight, nor NMR and UV-Vis spectroscopic behaviour. Using similar methodology, we have also prepared a liable tosyl-containing macromolecular derivative **11** that can be employed to yield tailored light and moisture stable aryl/alkylalkoxy substituted materials following replacement of the tosyl group.

2. Results and Discussion

2.1 Preparation and Characterization of Monomers

Compound **4** (Scheme 1) was prepared via a hydrostannylation reaction of allyl alcohol with Ph₃SnH in the presence of AIBN, and after washing the resulting solids with hexanes, isolated as a white coloured powder in an 82% yield. The NMR (¹H, ¹³C) spectroscopic data obtained for **4** was comparable to values previously reported by Wardell *et al.*^[36] In addition, the ¹¹⁹Sn NMR (CDCl₃) spectrum of **4** shows a single resonance at $\delta = -99.2$ ppm, which is similar to that of other previously reported propyloxy triphenylstannanes.^[11,17]



Scheme 1: Preparation of functional stannane monomers 6 and 9 via 4.

Dichlorido compound **5** was synthesized via a stepwise chlorination of **4** using 2 equivalents of HCl (1.0 M in Et₂O) in C₆H₆ over a 1 h (Scheme 1) time period. After the initial addition, the impure monochlorido (solid) intermediate was isolated but not fully characterized. This crude monochlorido was thereafter dissolved in DCM to separate it from the insoluble by-products prior to further chlorination. Identical reaction conditions were then used to generate the dichlorido **5**. The crude product was washed with hexanes (3×20 mL) to give **5** as pale yellow coloured solid in a 72% yield. NMR spectroscopic analysis of **5** (¹H, ¹³C: C₆D₆) is fully consistent with the expected structure. The ¹¹⁹Sn NMR (CDCl₃) resonance for **5** is slightly downfield (δ = -80.4 ppm) in comparison to that of **4**. Crystals of **5** suitable for X-ray diffraction were grown from a DCM solution containing **5** layered with hexanes (Figure 2a). The surmised 3c-4e sharing motif between the tin, chlorine, and oxygen atoms can be discerned from the molecular configuration.^[17] The propyl oxygen atom is found in a position strongly suggesting dative bonding to the Sn center with a notably shorter bond length (2.40 Å) when compared to

other previously reported five-coordinate Sn-O dichlorido species bearing either a propylazo or propylphenyl substituent (2.73 Å or 2.82 Å).^[17,37] The Sn-O bond length of **5** is about 17% larger than those reported for tin complexes ($2.05^{[38]}$ -2.14 Å^[39]) with truly covalent Sn-O bonds. In the hypercoordinated geometry of **5**, the axial Sn-Cl bond is notably elongated in comparison to the equatorial Sn-Cl bond (~0.09 Å) as expected (*vide supra*).



Figure 2a Left: ORTEP representation of 5 found in the unit cell and selected bond lengths (Å) and bond angles (°). Thermal ellipsoids drawn at the 30% level. Sn-O 2.400(3), Sn-Cl1 2.3766(14), Sn-Cl2 2.4509(12), Cl1-Sn-Cl2, 94.20(5), C1-Sn-C4 143.79(18), O-Sn-Cl2 173.88(9). 2b Right: ORTEP representation of 8 found in the unit cell and selected bond lengths (Å) and bond angles (°). Thermal ellipsoids drawn at the 30% level. Sn-O 5.418(3), Sn-Cl1 2.3660(6), Sn-Cl2 2.3776(6), Cl1-Sn-Cl2, 98.73(2), C1-Sn-C7 138.24(8), O1-S1-Cl0 105.88(9).

Compound **6** (Scheme 1) was synthesized through a standard hydrogenation of **5** with LiAlH₄ in Et₂O at 0°C for 4 h, after which the reaction was quenched with degassed distilled water. The desired compound was isolated in a 92% yield as a pale-yellow colored, translucent gel (Scheme 1). NMR spectroscopic analysis of **6** (¹H, ¹³C: CDCl₃) is consistent with the expected structure, including the large ^{117/119}Sn-H satellite coupling resonances (^{*1*}J = 1841 and 1926 Hz) centered on the hydrido signal ($\delta_{\rm H}$ = 5.51 ppm). The ¹¹⁹Sn NMR spectrum of **6** (C₆D₆) displayed a single resonance at δ = -214.9 ppm, a value typical for other known tin dihydrides.^[40] This thermally sensitive monomer was stored in the dark at -30 °C, and could be kept in this way for up to 30 days without substantial decomposition. The tosyl-containing triphenyl tin species **7** was prepared as previously described.^[17] Chlorination of **7** with HCl to give **8** proceeded in a single step in a nearly quantitative yield. Conversion of the tosylated tin dichlorido **8** to the dihydrido **9** was carried out with NaBH₄ and isolated after work up (see Experimental) in the form of a colourless liquid in a 62% yield. The hydrido resonance of **9** ($\delta_{H} = 5.31$ ppm) was found slightly upfield in comparison to **6**, with the ^{117/119}Sn-H couplings (¹*J* = 1764, 1852 Hz), smaller by about 70-80 Hz. Crystals of **8** suitable for X-ray diffraction were also grown from DCM solution containing the material layered with hexanes (Figure 2b). An intramolecular hypercoordinate interaction is clearly absent here, with the Sn-O distance of ~5.4 Å. The lack of an intramolecular dative interaction is likely related to the electron withdrawing strength of the tosyl substituent. There is no evidence of intermolecular interactions of the propyl oxygen with neighbouring tin centers in the unit cell, but one of the tosyl O atoms (O3) is oriented towards the Sn center of another molecule of **8** with an Sn-O distance of 2.776 Å and a O3-Sn-Cl2 angle of 176.3°. The geometry of the Sn center and near equivalence of the Sn-Cl bond lengths suggest however a relatively weak intermolecular interaction without substantial hypercoordinate character.

2.2 Computational studies of monomers

DFT calculations of monomers **5** and **8** were carried out for comparison with solid-state structural data to gain some insights into substituent effects. Such calculations are necessarily approximate: DFT optimized geometries are dependent on both the basis set and the functional used in the calculation and, once corrected for zero-point energy, correspond an isolated (gas-phase) molecule at 0 K. Calculation of thermodynamic properties is non-trivial, even for the gas phase, and especially for flexible molecules where Boltzmann conformational averaging is required. Despite these limitations, DFT calculations can be useful in comparisons between molecules or conformations, where relative differences are typically more accurately determined than absolute energies.

Due to the many possible conformations of the flexible monomers **5** and **8**, attention was restricted to the most stable of the non-hypercoordinate conformers, the *trans*-planar "open" conformer, and the hypercoordinate "closed" structures with phenyl and chlorido ligands respectively *trans* to a propyl oxygen atom (Figure 3). Dispersion-corrected B3LYP-GD3BJ geometry optimizations of each conformer were verified by frequency calculations. Table 2 presents energies for the hypercoordinate conformers relative to the respective "open" conformers.



"Open Conformer" "Closed Trans-Ph Conformer" "Closed Trans-Cl Conformer"

Figure 3. Optimized structures for conformations of **5** (B3LYP-GD3BJ/6-31+(d,p):H,C,O,Cl; LANL08d:Sn).

Table 2.	B3LYP-GD	O3BJ calcu	lated ene	ergies for	"closed"	'hyperco	oordinate	conformers	relative
to the res	pective "ope	en" confor	mers.						

Hypercoordinate conformer	Relative electronic energy [kJ mol ⁻¹]	Relative electronic and zero-point energies [kJ mol ⁻¹]
5: <i>trans</i> -phenyl	-18.4	-15.8
5: <i>trans</i> -chlorido	-40.6	-36.4
8: <i>trans</i> -phenyl	-13.0	-11.5
8: trans-chlorido	-37.1	-35.1

Hypercoordinate conformers are more stable than the "open" conformers in each case. Comparing the effect of the ligand *trans* to the hypercoordinate propyl oxygen shows significantly lower relative energies for conformers with the electronegative chlorido ligand (by $\sim 21 - 24 \text{ kJ mol}^{-1}$). Hypercoordinate conformers of **5** are somewhat more stable than **8** (by $\sim 3 - 5 \text{ kJ mol}^{-1}$), presumably due to greater electron density on the hypercoordinating O atom with a H substituent in comparison with the more electron-withdrawing tosyl substituent. Comparisons of calculated Sn-O distances support these observations. For the *trans*-phenyl conformer of 5, the Sn-O separation is 2.656 Å, while for the *trans*-chlorido conformer it is 2.572 Å. The hypercoordinate conformers of 8 have longer Sn-O distances in each case: 2.952 Å for the *trans*-phenyl conformer and 2.795 Å for the *trans*-chlorido conformer, but with the same trend with respect to the specific trans-ligand. Comparison of bond angles in the calculated structures of the hypercoordinated conformers with those of the open conformers show the expected shift towards trigonal bipyramidal geometries at Sn in the former, and to a greater degree with 5 than 8. In the two cases where comparisons of calculated and crystallographic structural parameters can be made, there is generally reasonable agreement. The calculated Sn-O separation distance is very similar for the "open" conformer of 8 and the somewhat different crystallographic conformer (5.418 Å (exp.), 5.444 Å (calc.)). In contrast, the "closed" trans-chlorido 5 crystallographic Sn-O distance is significantly shorter (2.400 Å) than the calculated one (2.572 Å), as has been noted previously for hypercoordinate Sn complexes.^[17] There are two other notable discrepancies in the calculated structures. The Cl-Sn-Cl bond angles are overestimated in the calculated "open" conformer of 8 by about 9°, possibly due to the intermolecular hypercoordinate interaction in the solid state noted above. Secondly, the calculated structure of 5 does not reproduce the long Sn-Cl bond length of the Cl *trans* to the hypercoordinate propyl O atom, a feature also noted previously.^[17] It is unclear whether this is a crystal packing effect or reflects an inadequacy in the computational model. This question remains an active area of investigation within our research group.

2.3 Polymerization and Characterization of Homopolymers 10 and 11



Accepted Manuscript

Scheme 2. Transition metal-catalyzed dehydropolymerization of tin dihydrides.

Homopolymers **10** and **11** were prepared via dehydropolymerization reactions of **6** and **9** involving the application of Wilkinson's catalyst in toluene at RT for 4 h (Scheme 2). Volatiles were thereafter removed *in vacuo* and the crude materials of **10** or **11** were then re-dissolved in a minimal volume of THF (3 mL) and added slowly, dropwise, to 100 mL of a stirring, cold hexanes mixture. The resulting yellow-coloured solids that formed were recovered by filtration, and after drying *in vacuo*, yellow coloured powders of purified **10** or **11** were recovered in a 78% and 63% yields, respectively. In the case of **10**, (Figure 4) a molecular weight determination (GPC) revealed a narrowly dispersed, modest molecular weight polymer (42 kDa; PDI 1.16). A lower molecular weight was found for **11** (31 kDa, PDI 1.20).

This article is protected by copyright. All rights reserved.



Figure 4. GPC chromatogram (RI, THF) of polystannanes 10 and 11.

¹H NMR (C₆D₆) analysis of **10** shows surprisingly well-resolved resonances for the aromatic and alkyl portions of the polymer; by contrast the ¹H NMR signals of purified **11** are notably broad. Interestingly, the ¹¹⁹Sn NMR spectrum of **10** in C₆D₆ displays two nearly equal intensity resonances ($\delta_{sn} = -113.4$ ppm and -176.0 ppm) (Figure 5b).



Figure 5. ¹¹⁹Sn NMR spectra of 10 and 11 in two deuterated solvents.

We attribute this to the presence of both an open (lower field) configuration, where propylhydroxy or propylalkoxy ligand is untethered to the tetrahedral tin centre, and a closed (higher field) motif where the –OH group is datively bound to the tin, making it formally 5-coordinate (Figure 6).



Figure 6. Proposed partially "open" and "closed" random structure of 10.

Interestingly, only a single sharp downfield resonance at -108 ppm was observed for polymer **10** when run in d⁸-THF (Figure 5a). The ¹¹⁹Sn NMR spectrum of **11** (Figures 5c, 5d) in either d^8 -THF or C₆D₆ are similar and reveal a broad spilt resonance centred near -202 ppm, which is

typical of chemical shifts of other polystannanes bearing propyloxy linkages.^[17,40] The differences in the ¹¹⁹Sn NMR between C_6D_6 and d⁸-THF are consistent with the relative coordinating ability of the related non-deutrated solvents as described by Alvarez et al.^[41] In the case of **10**, the d⁸-THF solvent likely overwhelms and displaces the intramolecular hypercoordinate bonding in the polymer so all propyloxy ligands lie in the open position.

Thermal analysis of **10** and **11** was conducted by DSC. Compound **10** was run through three consecutive heating/cooling cycles and showed no evidence of decomposition below 200 °C. A weak, reversible glass transition temperature (T_g) was detected at 49.3°C and a strong reversible melt temperature (T_m) was observed at 110.1 °C (Figure 7). These results suggest a semi-crystalline nature for polymer **10**. In the case of **11**, only a weak T_g (65.9 °C) was detected and is more typical of amorphous polymers (Figure B1).



Figure 7. DSC spectra for homopolymer 10.

An understanding of the morphology of polystannanes is of great interest because of the impact that hypercoordination in the solid state may have on the degree of crystallinity, and conjugation in the backbone. The suspected semi-crystalline polymer **10** was found to be both air and moisture stable. Analysis of the polymer morphology of **10** by PXRD without prior annealing, suggests some level of long range order, revealed by two broad peaks centered at $2\theta = 7.1^{\circ}$ and

 $2\theta = 19.7$ (Figure 8). This corresponds to possible interchain d-spacings of 4.51 Å and 12.5 Å respectively. The larger d-spacing is similar to that reported earlier by Caseri *et al.* (11.2-13.2 Å) for polymer **1**. Further work to explore the nature of these d-spacings is now ongoing.



Figure 8: The PXRD diffractogram of polymer 10.

3. Conclusions

The asymmetrical polystannane macromolecular intermediate **10** was prepared from the transition metal catalyzed dehydropolymerization of dihydrido **9** in a 78% yield. Characterization of **10** by ¹¹⁹Sn NMR spectroscopy in C₆D₆ revealed the presence of two equal intensity resonances at δ -117 and -175 ppm attributed to hyper and non-hypercoordinated Sn---O interactions along the polymer backbone. GPC analysis confirmed a narrowly dispersed high molecular weight polymer. Further analysis by DSC and PXRD revealed a semi-crystalline nature of **10**. Polymer **10** showed no evidence of decomposition after exposure to both ambient light and moist air for > 6 months. Polymer **11** bearing a tosyl substituent was also prepared by

dehydropolymerization, and could become an important macromolecular intermediate to a number of stable, asymmetrical polystannanes. These materials have obvious merit in the design of functional molecular wires containing polystannanes.

4.0 Experimental Section

Material and Methods. Syntheses were carried out using standard Schlenk and glove box protocols. ¹H NMR (400 MHz), ¹³C NMR (100.6 MHz), and ¹¹⁹Sn NMR (79.5 MHz) spectra for small molecules were recorded on a Bruker Avance 400 MHz NMR spectrometer with a BBFO 5 mm direct probe. A ¹H pulse width of 30° was used, acquiring a spectral window of 8223 Hz (20 ppm) using a relaxation delay of 1 s, acquisition time of 3.98 s, and 32k points (16 scans). The ¹H 90° pulse width was 10.4 μ s. A ¹³C pulse width of ¹H 30° pulse width was used acquiring a spectral window of 24,038 Hz (239 ppm) using a relaxation delay of 2 s, acquisition time of 1.36 s, and 32k points (4096 scans). The ${}^{13}C$ 90° pulse width was 8.7 µs. A ${}^{119}Sn$ pulse width of 30° was used, 8.75 µs, acquiring a spectral window of 100,000 Hz (670 ppm) using a relaxation delay of 1 s, acquisition time of 0.33 s, and 32k points (15,360 scans) with inverse gated proton decoupling. ¹H and ¹³C were referenced internally to the deuterated solvent resonances. All chemical shifts are given in δ (ppm) relative to the solvent and assigned to atoms. All J coupling values are reported as absolute values. Additional 1D ¹³C and ¹¹⁹Sn NMR data for polymers were acquired at the CSICOMP NMR facility at the University of Toronto. $1D^{13}C$ spectra were acquired using an Agilent DD2 spectrometer (n(^{13}C); 125.653 MHz, n(^{1}H); 499.663 MHz) equipped with either a 5 mm XSens ¹³C-sensitive Cold Probe (Agilent Technologies, Inc., Santa Clara, USA). The 1D ${}^{13}C{}^{1}H{}$ spectra were acquired with a standard CARBON pulse sequence at 25 °C, over a 30487.8 Hz spectral window with a 30° pulse width, 121952 points, a 0.2 s recycle delay, and 3200 transients. 1D ¹¹⁹Sn spectra were acquired using an Agilent DD2 spectrometer (n(¹¹⁹Sn); 186.378 MHz, n(¹H); 499.875 MHz) equipped with a OneNMR probe (Agilent Technologies, Inc., Santa Clara, USA). The 1D¹¹⁹Sn{¹H} spectra were acquired with an s2pul pulse sequence at 25 °C, over a 56818.2 Hz spectral window with a 45° pulse width, 113636 points, a 1.0 s recycle delay, and 5000 transients. Inverse gated proton decoupling was applied. Elemental analysis was performed by Atlantic Microlab, Inc. of Norcross, GA, USA. Time-of-flight mass spectrometry analyses were performed using a JMS-T1000LC mass spectrometer (JEOL Inc., Peabody, MA, USA) equipped with a direct analysis in real time (DART) ionization source (DART-SVP, Ionsense Inc., Saugus, MA, USA) at University of Toronto. The DART source was operated with He gas, and the temperature was adjusted in the range 100-400 °C. Isotopic distributions for the observed ionic species were calculated using the Mass Center utility (JEOL) and were in good agreement with the measured mass spectra. All reagents and solvents were obtained from Sigma-Aldrich and used as received. Triphenyl tin chloride was purchased from Sigma-Aldrich. Triphenylstannane was prepared and characterized according to published routes. All column chromatography was carried out on Silica gel or 60 aluminum backed plates, eluting with the solvent system indicated below for each compound. Melting points were measured in open air using a Fischer Scientific melting point apparatus. Molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Viscotek Triple Model 302 Detector system equipped with a Refractive Index Detector (RI), a four capillary differential viscometer (VISC), a right angle (90°) laser light scattering detector. GPC columns were calibrated versus polystyrene standards (American Polymer Standards). A flow rate of 1.0 mL min⁻¹ was used with ACS grade THF as eluent. GPC sample were prepared using 10-15 mg of polymers per mL THF, and filtered using a 0.45 µm filter. All UV-VIS spectroscopy were carried out using a Perkin Elmer Lambda 40 UV/Vis system. The University of Toronto X-ray Crystallography Lab was used to obtain Xray information for compounds 5 and 8. Data was collected on a Bruker Kappa APEXDUO diffractometer using monochromated Mo-Ka radiation (Bruker Triumph) and were measured using a combination of φ scans and ω scans. The data was processed using APEX2 and SAINT1. Absorption corrections were carried out using SADABS.1. The structures were

Accepted Manuscript

solved using SHELXT2 and refined using SHELXL-20132 for full-matrix least-squares refinement that was based on *F*2. For all structures, H atoms were included in calculated positions and allowed to refine in a riding-motion approximation with U~iso~ tied to the carrier atom. All geometric optimizations and frequency calculations were carried out with the Gaussian 09 suite of programs^[42] using the B3LYP level of theory^[43] supplemented with Grimme's D3 empirical dispersion function and Becke-Johnson damping.^[44] The LANL08d basis set was used for Sn^[45] and the 6-31+G(d,p) basis set for all other atoms, as a reasonable compromise between accuracy and computational cost.^[46,47] Tight convergence criteria and an ultrafine integration grid were employed for all geometry optimizations. Frequency calculations were performed in each case to verify that a minimum in the potential energy surface had been located.

Synthesis of 3-(Triphenylstannyl)propan-1-ol (4)

Propa-2-ene-1-ol (0.8 mL, 13.7 mmol) was added to a dry 50 mL Schlenk flask *via* syringe. Ph₃SnH (1.46 g, 4.15 mmol) and 2% mole AIBN (0.045 g, 0.274 mmol) was added to the allyl alcohol. The flask was heated to 80°C for 3 h. A white colored solid formed when the solution cooled. The crude sample was washed with hexanes (3 × 10 mL) and the white colored solid was isolated by vacuum filtration. Synthesis was previously reported by Wardell *et al.*^[36] Yield 82.2% (1.39 g); m.p. 105°C. ¹H NMR (400 MHz, C₆D₆, δ): 7.60-7.54 (m, 6H, H6), 7.39-7.35 (m, 9H, H7 & H8), 3.64 (t, 2H, H2, ³J = 6.6 Hz), 2.01-1.94 (m, 2H, H3), 1.55-1.49 (m, 2H, H4) ppm, 1.29 (s, 1H, H1). ¹³C{¹H} NMR (100 MHz, C₆D₆, δ): 138.99 (C5), 137.04 (C6), 128.84 (C8), 65.66 (C2) 29.36 (C3), 6.67 (C4) ppm. ¹¹⁹Sn NMR (149 MHz, CDCl₃, δ): -99.16 ppm.

Synthesis of 3-(dichloro(phenyl)stannyl)propan-1-ol (5)

In a 100 mL dry Schlenk flask, 1.0 M HCl/Et₂O (2.45 mL) was added to a solution of **4** in C_6H_6 (25 mL). This was repeated for a second time for full conversion. The mixture was stirred at

- 19 -

RT for 1 h and the solvent removed *in vacuo* to obtain a pale yellow colored powder of **5**. The crude product was washed with hexanes $(3 \times 20 \text{ mL})$ and brought to dryness. Yield 72.1% (0.919 g); m.p. 96.5°C. ¹H NMR (400 MHz, C₆D₆, δ): 7.89-7.70 (m, 2H, H6), 7.55-7.36 (m, 3H, H7 & H8), 3.85 (s, 2H, H2), 2.86 (s, 1H, H1), 2.17-2.14 (m, H3, 2H), 1.87 (t, 2H, H4, ³*J* = 6.9 Hz) ppm. ¹³C{¹H} NMR (100 MHz, C₆D₆, δ): 141.27 (C5), 135.27 (C6), 130.79 (C7), 129.10 (C8), 129.10 (C8), 62.57 (C2). ¹¹⁹Sn NMR (149 MHz, CDCl₃, δ): -80.48 ppm. HRMS-DART (m/z) = 290.9599 (M-Cl) calculated for ¹²C₉¹H₁₂¹⁶O₁³⁵Cl₂¹²⁰Sn₁; found 290.9588.

Synthesis of 3-(phenylstannyl)propan-1-ol (6)

A solution of **5** (0.73 g, 2.24 mmol) in Et₂O (5 mL) was added to a solution of 1 M LiAlH₄/Et₂O (2.24 mL) in Et₂O (10 mL) in 100 mL Schlenk flask at 0°C. After 4 h, the reaction was warmed to room temperature and distilled degassed water (12 mL) was added to the solution to quench the reaction. The organic layer was removed, and the solvent was removed under reduced pressure to obtain a pale-yellow colored, translucent gel of **6**. Yield 92.1% (0.53 g). ¹H NMR (400 MHz, C₆D₆, δ): 7.47-7.39 (m, 2H, H6), 7.17-7.11 (m, 3H, H7 & H8), 5.51 (s, 2H, H9, ^{117Sn-H}*J* = 1841 Hz, ^{119Sn-H}*J* = 1926 Hz), 3.35 (t, 2H, H2, ³*J* = 6.27 Hz), 2.60 (s, 1H, H1), 1.71-1.64 (m, 2H, H3), 1.08-1.00 (m, 2H, H4) ppm. ¹³C{¹H} NMR (100 MHz, C₆D₆, δ): 137.44 (C6), 128.52 (C7 & C8), 64.76 (C2), 30.12 (C3), 4.41 (C4, ^{117/119Sn-C}*J* = 401.3 Hz) ppm. ¹¹⁹Sn NMR (149 MHz, C₆D₆, δ): -214.89 ppm. HRMS-DART (m/z) = 256.9988 (M+H) calculated for ¹²C₉¹H₁₄¹⁶O₁¹²⁰Sn₁; found 256.9991.

Synthesis of (Triphenylstannyl)butyl 4-methylbenzenesulfonate (7)

Compound 7 was prepared as previously reported.^[17]

Synthesis of 4-(dichloro(phenyl)stannyl)butyl 4-methylbenzenesulfonate (8)

3-(Triphenylstannyl)propyl 4-methylbenzenesulfonate, **7**, (0.1 g, 0.178 mmol) in C₆H₆ (\approx 20 mL) was added 1.0 M HCl/Et₂O (0.18 mL, 0.178 mmol) by syringe and stirred at 0°C for 1 h. The pure product was then precipitated in to a large volume of hexane (100 mL) with stirring.

- 20 -

After decanting, the residual solvent was removed *in vacuo* to obtain a white colored solid of **8** in near quantitative yield. Yield 99 % (0.20 g); m.p. 102 °C. ¹H NMR (400 MHz, CDCl₃, δ): 7.80-7.74 (m, 2H, H8), 7.74-7.73 (m, 2H, H7), 7.72-7.52 (m, 3H, H6 & H5), 7.34-7.32 (m, 2H, H9), 4.15-4.13 (t, ³*J* = 5.5 Hz, 2H, H4), 2.44 (s, 3H, H3), 2.26-2.23 (t, ³*J* = 12.5 Hz, 2H, H2), 1.97-1.94 (t, ³*J* = 7.6 Hz, 2H, H1) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃, δ): 145.18 (C10), 138.73 (C12), 134.88 (C11), 132.55 (C7), 131.60 (C9), 130.02-129.56 (C5 & C6), 128.02 (C8), 71.18 (C4), 24.57 (C3), 21.71 (C2), 21.07 (C1) ppm; ¹¹⁹Sn NMR (79.5 MHz, CDCl₃, δ): 30.1 ppm. EA C_{calc/found}: 40.04/41.40, H_{calc/found}: 3.78/3.87

Synthesis of 3-(phenylstannyl)propyl 4-methylbenzenesulfonate (9)

An EtOH solution (10 mL) containing **8** (0.21 g, 0.438 mmol) was added to a solution of NaBH4 (0.150 g, 4.38 mmol) in EtOH (8 mL) in a 100 mL Schlenk flask, and stirred at 0 °C for 1 h. 20 mL of 5°C degassed distilled water was added to the solution containing crude **9** over 30 min and stirred. The solution was then extracted with hexanes (3 × 20 mL) and dried over MgSO4. The mixture containing **9** was filtered, and solvent removed under reduced pressure to obtain a transparent colorless liquid. Yield 62 % (0.111 g). ¹H NMR (400 MHz, C₆D₆, δ): ¹H NMR (400 MHz, CbCl₃, δ): 7.75-7.73 (m, 2H, H8), 7.40-7.31 (m, 2H, H7), 7.14-7.13 (m, 3H, H6 & H5), 6.73-6.71 (m, 2H, H9), 5.31 (s, ^{117Sn-H}*J* = 1764 Hz, ^{119Sn-H}*J* = 1851.6 Hz, 2H, H13), 3.74-3.71 (t, ³*J* = 6.3 Hz, 2H, H4), 1.85 (s, 3H, H3), 1.54-1.47 (q, ²*J* = 13.9 Hz, ¹*J* = 7.2 Hz, 2H, H2), 0.74-0.70 (t, ³*J* = 8.2 Hz, 2H, H1) ppm; ¹³C{¹H} NMR (100 MHz, C₆D₆, δ): 143.87 (C10), 137.32 (C12), 135.39 (C11), 134.22 (C7), 129.43 (C9), 128.67-128.42 (C5 & C6), 127.81 (C8), 71.85 (C4), 26.81 (C3), 20.76 (C2), 3.17 (C1) ppm; ¹¹⁹Sn NMR (79.5 MHz, C₆D₆, δ): -216.2 ppm. HRMS-DART (m/z) = 411.00769 (M+H) calculated for ¹²C₁₆¹H₂₀¹⁶O₃³²S₁¹²⁰Sn₁; found 411.00809.

Chemistry - A European Journal

Preparation of hydroxy homopolymer (10)

A solution of toluene (10 mL) and RhCl(PPh₃)₃ (0.076 g, 0.082 mmol) was added to a foil wrapped 100 mL Schlenk flask. The solution mixture was stirred at RT for 10 min to activate the catalyst. A solution of **6** (0.53 g, 2.06 mmol) in toluene (5 mL) was added to the catalyst solution, and the reaction allowed to stir at RT for 4 h. The solvent was removed *in vacuo* and the crude product was dissolved in minimal amount of THF (< 1 mL) and transferred dropwise to a 100 mL flask containing a stirring solution of cold hexanes (50 mL). A yellow colored precipitate formed immediately, and the solution was stirred for an additional 5 min and allowed to settle. The hexane layer was removed with a Pasteur pipette. The solid was dried *in vacuo* to obtain a dry yellow colored powder of **10**. Yield = 78%. M_w = 42,000 Da, PDI = 1.16. ¹H NMR (400 MHz, C₆D₆, δ): 7.59-6.95 (m, 5H, H6-H8), 3.57-3.54 (m, 2H, H2), 1.28-1.22 (m, 2H, H3), 0.89-0.82 (m, 2H, H4) ppm. ¹³C{1H} NMR (100 MHz, C₆D₆, δ): 139.06 (C7), 133.25 (C8), 132.93 (C5), 130.02 (C6), 69.39 (C2), 31.64 (C3), 27.31 (C4) ppm. ¹¹⁹Sn NMR (149 MHz, C₆D₆, δ): -113.42 & -176.13 ppm. EA C_{calc/found}: 42.41/39.52, H_{calc/found}: 4.75/4.54

Preparation of tosyl-polymer (11)

A toluene solution (9 mL) containing RhCl(PPh₃)₃ (0.0320 g, 0.0350 mmol) was added to a foil wrapped 50 mL Schlenk flask and stirred at 0 °C (20 min) for activation. Thereafter, **9** in 9 mL of toluene (0.360 g, 0.876 mmol) was added dropwise over 20 min to the catalyst solution. The reaction was allowed to stir at 0 °C for 4 h. The mixture was then reduced in volume (*in vacuo*) to roughly 5 mL and using a double tipped cannula, transferred to a 100 mL foil wrapped Schlenk flask contained a stirring solution of cold hexanes (50 mL). An orange-yellow precipitate formed immediately and the solution was stirred for additional 5 min and then allowed to settle. The top layer of the solution was then extracted using a double tipped cannula needle. The residues were dried *in vacuo* to obtain an orange yellow coloured solid. Yield 63 %

(0.230 g). $M_w = 31,000$ Da, PDI = 1.20. ¹H NMR (400 MHz, C₆D₆, δ): 7.91 (bm, 2H, H8), 7.76-7.37 (bm, 5H, H5-H7), 6.88-6.83 (bm, 2H, H9), 3.73 (bm, 2H, H4), 1.88-1.54 (bm, 5H, H2 & H3), 1.23 (bm, 2H, H1) ppm; ¹³C{1H} NMR (100 MHz, C₆D₆, δ): 144.10 (C10), 138.15 (C12), 137.12 (C6), 133.84 (C11), 133.82 (C7), 131.96 (C9), 126.33 (C8), 72.98 (C4), 29.55 (C2), 21.17 (C1), 14.02 (C3) ppm; ¹¹⁹Sn NMR (79.5 MHz, C₆D₆, δ): -205 ppm. EA C_{calc/found}: 46.98/45.45, H_{calc/found}: 4.44/4.30

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. Crystallographic data for compounds **5** (CCDC# 1843959) and **8** (CCDC# 1843959) were deposited with the Cambridge Crystallographic Data Base.

Acknowledgements: This work was funded by the NSERC Discovery Grant Program. The computational studies were made possible by the facilities of the Shared Hierarchical Academic Research Computing Network (SHARCNET: <u>www.sharcnet.ca</u>) and Compute/Calcul Canada. Thanks to Prof. Robert Gossage for his kind and timely editing of this manuscript.

Received: Month XX, XXXX; Revised: Month XX, XXXX; Published online:

Keywords: hypercoordinate, polystannanes, tin dihydrides, dehydropolymerization

- H. K. Sharma, K. H. Pannell, in *Tin Chem. Fundam. Front. Appl.* (Eds.: A.G. Davies,
 M. Gielen, K.H. Pannell, E.R.T. Tiekinh), John Wiley & Sons Ltd., 2008, pp. 376–391.
- [2] D. A. Foucher, in *Catenated Ger. Tin Oligomers Polym.* (Eds.: T. Baumgartner, F. Jäkle), John Wiley & Sons Ltd., Hobeken, NJ, **2018**, pp. 209–236.
- [3] W. Caseri, *Chem. Soc. Rev.* **2016**, *45*, 5187–5199.

- 23 -

- [4] T. Imori, T. D. Tilley, J. Chem. Soc. Chem. Commun. 1993, 1607–1609.
- [5] T. Imori, V. Lu, H. Cai, T. D. Tilley, J. Am. Chem. Soc. 1995, 117, 9931–9940.
- [6] V. Y. Lu, T. D. Tilley, *Macromolecules* **2000**, *33*, 2403–2412.
- [7] F. Choffat, P. Smith, W. Caseri, J. Mater. Chem. 2005, 15, 1789–1792.
- [8] M. Trummer, F. Choffat, P. Smith, W. Caseri, *Macromol. Rapid Commun.* 2012, *33*, 448–460.
- [9] F. Choffat, S. Kaeser, P. Wolfer, D. Schmid, R. Mezzenga, P. Smith, W. Caseri, *Macromolecules* 2007, 40, 7878–7889.
- [10] N. Devylder, M. Hill, K. C. Molloy, G. J. Price, *Chem. Commun.* **1996**, 711–712.
- [11] P. R. Deacon, N. Devylder, M. S. Hill, M. F. Mahon, K. C. Molloy, G. J. Price, J. Organomet. Chem. 2003, 687, 46–56.
- [12] M. Trummer, J. Zemp, C. Sax, P. Smith, W. Caseri, J. Organomet. Chem. 2011, 696, 3041–3049.
- [13] M. Okano, N. Matsumoto, M. Arakawa, T. Tsuruta, H. Hamano, *Chem. Commun.* 1998, 1799–1800.
- [14] M. Okano, K. Watanabe, *Electrochem. Commun.* **2000**, *2*, 471–474.
- [15] S. Harrypersad, D. Foucher, *Chem. Commun.* **2015**, *51*, 7120–7123.
- [16] D. Miles, T. Burrow, A. Lough, D. Foucher, J. Inorg. Organomet. Polym. Mater. 2010, 20, 544–553.
- [17] J. Pau, R. A. Gossage, R. S. Wylie, A. J. Lough, D. A. Foucher, *Chem. A Eur. J.* **2017**, *57*, 14367–14374.
- [18] F. Choffat, P. Wolfer, P. Smith, W. Caseri, *Macromol. Mater. Eng.* 2010, 295, 210–221.
- [19] M. Trummer, T. Nauser, M.-L. Lechner, F. Uhlig, W. Caseri, *Polym. Degrad. Stab.* **2011**, *96*, 1841–1846.
- [20] V. Lu, T. D. Tilley, *Macromolecules* **1996**, *29*, 5763–5764.

- [21] F. Choffat, Y. Buchmueller, C. Mensing, P. Smith, W. Caseri, J. Inorg. Organomet. Polym. Mater. 2009, 19, 166–175.
- [22] D. Miles, T. Burrow, A. Lough, D. Foucher, J. Inorg. Organomet. Polym. Mater. 2010, 20, 544–553.
- [23] K.-Y. Akiba, Chemistry of Hypervalent Compounds, John Wiley & Sons, Ltd., New York, 1999.
- [24] A. Khan, D. A. Foucher, *Coord. Chem. Rev.* **2015**, *312*, 41–66.
- [25] S. N. Tandura, M. G. Voronkov, N. A. Alekseev, Top. Curr. Chem. 1986, 131, 99–189.
- [26] C. Chuit, R. J. P. Corriu, C. Reye, J. C. Young, *Chem. Rev.* **1993**, *93*, 1371–1448.
- [27] R. R. Holmes, Chem. Rev. 1996, 96, 927–950.
- [28] M. G. Voronkov, O. M. Trofimoua, Y. I. Bulgova, N. F. Chernov, *Russ. Chem. Rev.* 2007, 76, 825–845.
- [29] Y. I. Baukov, S. N. Tandura, Z. Rappoport, *The Chemistry of Organic Germanium, Tin and Lead Compounds*, John Wiley & Sons, Ltd., New York, 2002.
- [30] J. T. B. H. Jastrzebski, G. van Koten, Adv. Organomet. Chem. 1993, 35, 241–294.
- [31] M. J. Janseen, J. G. A. Lujiten, G. J. M. van der Kerk, J. Organomet. Chem. 1964, 1, 286–291.
- [32] T. I. R. Beattie, T. Gilson, J. Chem. Soc. 1961, 2585–2586.
- [33] J. I. Musher, Angew. Chem. Int. Ed. Engl. 1969, 8, 54–68.
- [34] A. Khan, A. Patel, S. Komejan, C. Lombardi, A. J. Lough, D. A. Foucher, J. Organomet. Chem. 2015, 776, 180–191.
- [35] N. R. Neale, T. D. Tilley, J. Am. Chem. Soc. 2002, 124, 3802–3803.
- [36] J. L. Wardell, J. M. Wigzell, J. Chem. Soc. Dalt. Trans. 1982, 2–7.
- [37] T. Munguia, M. López-Cardoso, F. Cervantes-Lee, K. H. Pannell, *Inorg. Chem.* 2007, 46, 1305–1314.
- [38] L. E. Sutton, Tables of Interatomic Distances and Configurations in Molecules and

10.1002/chem.201804145

Ions: Supplement 1956-1959, Chemical Society, London, 1965.

- [39] J. B. Hall, D. Britton, Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem. 1972, 28, 2133–2136.
- [40] A. Khan, S. Komejan, A. Patel, C. Lombardi, A. J. Lough, D. A. Foucher, J. Organomet. Chem. 2015, 776, 180–191.
- [41] R. Diaz-Torres, S. Alvarez, *Dalt. Trans.* 2011, 40, 10311–10315.
- [42] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**
- [43] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, J. Phys. Chem. 1994, 98, 11623–11627.
- [44] S. Grimme, S. Ehrlich, L. Goerigk, J. Comp. Chem. 2011, 32, 1456–1465.
- [45] L. E. Roy, P. J. Hay, R. L. Martin, J. Chem. Theory Comput. 2008, 4, 1029–1031.
- [46] S. R. Whittleton, R. J. Boyd, T. B. Grindley, J. Phys. Chem. A 2006, 110, 5893–5896.
- [47] P. Matczak, Comput. Theor. Chem. 2012, 983, 25–30.

Table of Contents Entry

Synthesis and Characterization of Readily Modified Poly(aryl)(alkoxy)stannanes by use of Hypercoordinate Sn Monomers

Jeffrey Pau, Gloria M. D'Amaral, Alan J. Lought, R. Stephen Wylie, and Daniel A. Foucher *



A simple light and moisture stable semi-crystalline hypercoordinate polystannane is revealed. A key design feature for asymmetrical polystannanes is the use of strongly datively bonded ligands that render a majority of tin(IV) centers of this main group inorganic polymer 5-coordinate, electron rich and protected from nucleophilic attack.