CHEMISTRY A European Journal



Accepted Article Title: Proof of Concept Studies Directed Towards Designed Molecular Wires: Property Driven Synthesis of Air and Moisture-Stable Polystannanes Authors: Daniel Foucher, Jeffery Pau, Alan J Lough, Robert Steven Wylie, and Robert A Gossage 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.201703453 Link to VoR: http://dx.doi.org/10.1002/chem.201703453

Supported by ACES



FULL PAPER

Proof of Concept Studies Directed Towards Designed Molecular Wires: Property Driven Synthesis of Air and Moisture-Stable Polystannanes

Jeffrey Pau,^[a] Alan J. Lough,^[b] R. Stephen Wylie,^[a] Robert A. Gossage,^[a] and Daniel A. Foucher*^[a]

Abstract: Polystannanes with azobenzene moieties designed to protect the Sn-Sn backbone from light- and moisture-induced degradation is described. The azo-stannyl precursor 3 (70%) is converted in good yields (88-91%) to the mono- (4), and dichloro- (5) stannanes, by sequential chlorination, followed by further reduction of 5 to the dihydride (6) using NaBH₄ (78%). All stannanes were characterised by NMR (¹H, ¹³C, ¹¹⁹Sn) spectroscopy and HRMS; in addition, 3, 4 and 5 were structurally elucidated via X-ray diffraction analysis. Metal-free dehydrocoupling of 6 at RT leads exclusively to homopolymer (7-i) displaying an initial solution ¹¹⁹Sn NMR signal (δ = -196 ppm) that migrates to -235 ppm after 10 days (7-f). In contrast, metal-catalyzed dehydrocoupling of 6 in toluene at RT leads directly 7-f. Random co-polymers formed from 6 and (n-Bu)₂SnH₂ at 4:1 (8a) and 1:1 (8b) ratios were compared to the alternating polystannane (9) prepared by the reaction of 6 with (n-Bu)₂Sn(NEt₂)₂. DFT calculations of 3-6 indicate that hypercoordination at Sn is influenced by substituents and by solvation. Homopolymer 7 was found to have unprecedented moisture and light stability in the solid state for > 6 months.

Introduction

As electronic components become increasingly reduced in size, the need for "molecular wire"^[1] interconnects in the same dimension becomes essential.^[2] Molecular or polymeric wires would ideally be air-stable, easily processed or printed, flexible nano-materials consisting of a single chain of atoms.^[3] This chain would be capable of electron transport along the backbone and ideally exhibit excellent conductive properties. A further advantage would be their production from elements that are high in natural abundance and potentially recyclable. The bonding in all later Group 14 homopolymers (i.e., Si, Ge or Sn-based) feature, along the polymer backbone, extensive σ - σ overlap of the (formally) large and diffuse sp³ metal-centred hybrid orbitals.^[4-7] The unique structural and electronic configuration(s) in these homopolymers results in relatively narrow band gaps (2-4 eV) and a visible σ - σ * absorption related to their pronounced semi-conducting nature. The incorporation of aromatic groups onto the Group 14 element, most notably in the case

[a]	J. Pau, Prof. R. S. Wylie, Prof. R. A. Gossage, Prof. D. A. Foucher
	Department of Chemistry and Biology
	Ryerson University, Toronto, Ontario Canada
	350 Victoria Street, M5B 2K3
	E-mail: daniel.foucher@ryerson.ca
[b]	Dr. Alan J. Lough,
	Department of Chemistry
	University of Toronto, Toronto, Ontario Canada
	80 St. George Street, 2M5S 3H6
	Supporting information for this article is given via a link at the end of the document

of tin, provides additional $\sigma-\pi$ delocalization, typically resulting in a redshift of the visible absorption.^[8] The intriguing electronic properties of catenated stannanes come at the expense of long and relatively weak bonds between tin centres. Previous solution and solid state stability studies of polystannanes reveal that they readily degrade into smaller tin oligomers or cyclic species when exposed to visible light (350–500 nm) even for very short time periods.^{[9],[10]} Although stable to oxidation, polystannanes are readily hydrolyzed to linear and cyclic oligostannoxanes when exposed to moist air.^[11]

We have recently shown that the overall chemical and photostability of polystannanes can be enhanced with the incorporation of flexible hyper-coordinated (e.g., five-coordinate) tin centers.^[12] This change in coordination number from four to five is surmised to decrease the Lewis acidity at tin; this in turn leads to an increase in light stability (> 90 d)^[12] and a modest improvement with respect to hydrolysis. This platform utilizes a non-rigid hydrocarbon-based chain connected to an aryl or biaryl unit via an ether linkage. This latter functionality was designed to promote *O*-chelation and provide steric bulk.

To further enhance the stability of polystannanes, the application of a similar bulky alkoxy group, however now incorporating an azobenzene moiety, is herein investigated. Azobenzenes are biaryl species linked by a -N=N- bridge,^[13] and absorb specific wavelengths of visible light while transmitting or reflecting others.^[14] Azobenzenes are highly coloured and used extensively in the food, drug and cosmetics industries and account for approximately 60% of the worlds' production of industrial dyes.^{[14],[15]} Azobenzenes have also recently been incorporated for use in dyesensitized solar cells and in the prototyping of high density solar thermal cells.[16] Barrett and others have also successfully demonstrated the harnessing of photomechanical energy of azo-functionalized "walking" polymers; and has further described their suitability as key components for light driven plastic motors.^[17] We envisioned that this light absorbing unit might lead to greatly enhanced polystannane stability with respect to the simple aryl or biaryl groups that we previously studied.[9]

FULL PAPER



Figure 1. The light-induced trans-/cis- (i.e., (E)/(Z)) isomerisation of azobenzene.

An important characteristic of the azobenzene class of molecules is the photoisomerization between the cis- and trans- (i.e., (Z) to (E)) forms (Figure 1). The (E)-isomer is rapidly converted to the (Z)-form when exposed to light wavelengths between 320-350 nm. Absorption bands equivalent to the $S_0 \rightarrow S_2$ state are employed, corresponding to the energy gap of a $\pi - \pi^*$ symmetry-allowed transition. The reaction is fully reversible and the (E)-isomer is regenerated when the more sterically hindered (Z)compound is exposed to either visible light (400-450 nm) or by the application of heat.^[18] This (Z)- to (E)- conversion results in absorption bands equivalent to the $S_0 \rightarrow S_1$ state and correspond to the energy gap of a $n-\pi^*$ symmetryforbidden transition.

This investigation involves a multi-step preparation of an azobenzene-stannyl dihydride monomer, which is subsequently polymerised to azobenzene containing homoand co-polymers via dehydropolymerisation. A second polystannane of the alternating copolymer class, also containing an azobenzene functionality, was prepared by a complimentary condensation method. The bulky azobenzene unit was designed to serve two purposes: 1) to act as a "photoantenna" whose purpose is to absorb and/or reflect visible and UV light energy with the function of reducing photoscission events along the polystannane chain; and 2) to incorporate steric bulk and potential ligation to facilitate protection of the Sn backbone from nucleophilic attack. In this regard, the characteristic (Z)/(E)photoisomerization of the azobenzene chromophore in proximity to either a four- or five-coordinate geometry in all tin species is revealed. In addition, oligomeric and polymer models and complete characterization of monomer and premonomer compounds is supplemented by DFT calculations and UV-Vis spectroscopy where appropriate.

Results and Discussion

Synthesis

Alcohol 1 (Scheme 1) has been previously described by Wardell et al.[19] using a preparation involving the treatment of Ph₃SnH and an excess of allyl alcohol (in a solventless environment) at 80-95 °C in the presence of AIBN. This gives 1 in modest yields (~58%). In our hands, the same reaction conditions were followed

except we have found that a slight modification greatly improves product yields. Hence, the reaction was carried out in a sealed flask, recovering 1 as a white coloured solid in quantitative vield.^[16] The attempted tosylation of **1** using Christoffers et al. procedure (employing pyridine: RT; 5h) was unsuccessful and resulted in only the recovery of starting materials.^[16] However, tosylation of 1 to 2 can be achieved (60%) in a 2 h time frame using Yoshida's procedure (Scheme 1),^[20] wherein a catalytic amount of the ammonium salt, Me₃N•HCl, along with NEt₃, are added to the reaction mixture.



Scheme 1. Tosylation conditions used to prepare 2.

Initial efforts to prepare 3 (Scheme 2) via substitution of 4-hydroxyazobenzene (HAB) with allyl bromide, followed by hydrostannylation with Ph₃SnH, were not successful. However, the synthesis of 3 can be achieved by reacting HAB with 2 under S_N2 displacement conditions.^[21] This column process results in the recovery, after chromatography, of an air and moisture stable orange coloured solid 3 (70%).



Scheme 2. S_N2 Displacement reaction leading to 3.

Compound 3 was subsequently converted via stepwise chlorination (Scheme 3) to the mono- (4), and dichlorostannanes (5) in good yields (88% and 91%, respectively) without the need for column chromatography.^[22] Following

FULL PAPER

conditions traditionally used to obtain tin dihydrides, **5** was reacted with LiAlH₄ (Et₂O: 0 °C; 3 h). However, this potent source of H⁻ appeared to decompose the starting material. When a more moderate hydrogenating agent, NaBH₄, was used **5** was cleanly converted to **6** (78%) and thereafter isolated as an orange-yellow coloured powder (Scheme 3).

NMR Spectroscopy

The ¹H NMR (CDCl₃) spectra of **3-6** (Table 1) display three distinct sets of methylene resonances with large ^{119/117}Sn-H coupling constants (J) observed for the CH₂-Sn resonance. The Sn-H resonance signal of 6 is observed at 5.51 ppm, with distinct ^{119/117}Sn satellites (${}^{1}J^{119}Sn - {}^{1}H = 918$ Hz, ${}^{1}J^{117}Sn ^{1}$ H = 878 Hz). The methylene protons in **6** are shifted upfield in comparison to 3 and the chloro-containing stannanes 4 and 5. Interestingly, the ¹H NMR of 6 also indicates that two isomeric species are present in solution. The ¹H NMR of 6 taken initially t = 0, 6 and 24 h are shown in Figure S1 and displaying isomer ratios of 10:1, 4:1 and 1:1 respectively. In contrast, the corresponding ¹¹⁹Sn NMR signals at t = 0, 6and 24 h show no change in the tin resonance behaviour and this value is typical of a four-coordinate tin dihydride species.^[23] We therefore ascribe these observations as likely being related to a light induced (E)/(Z) isomerization of the azobenzene fragment. The ¹¹⁹Sn NMR resonance for 3 is found at δ = -100 ppm, a value typical of tetrahedrally coordinated organotins.^[21] By comparison, the ¹¹⁹Sn NMR resonances for 4 and 5 are significantly deshielded ($\delta = -15.3$ ppm and δ = -9.06 ppm, respectively). These downfield resonances are more consistent with a five-coordinate geometry for both 4 and 5 in solution.^[24]

Further evidence for the preferred geometries of compounds **3**, **4** and **5** was obtained by single crystal X-ray diffraction studies (see appendices B1, B2 and B3).



Scheme 3. Stepwise chlorination of 3 to 4 and 5, and hydrogenation to 6.

		¹ H NMR (ppm)		¹¹⁹ Sn NMR (ppm)	
	Sn-C H ₂	Sn-CH ₂ -C H ₂ - CH ₂ O	C H 2-O		
3*	1.66	2.25	4.03	-99.7	
4*	1.94	2.43	4.14	-15.3	
5*	2.18	2.56	4.22	-9.06	
6**	1.02	1.80	3.46	-214.5	

The tin atoms of both conformers observed in the solid-state of **3** (Figure 2) are pseudo-tetrahedral ($\tau_4 = 0.85$, $\tau_4' = 0.87$)^[25] with a Sn to O distance of ~4.9 Å, which lies well outside of the sum of the van der Waals radii (Sn-O 2.3 Å). In contrast, the mono-**4**, and dichloro species **5** (Figures 3 and 4) are formally five-coordinate (**4**: $\tau_5 = 0.85$, **5**: $\tau_5 = 0.46$)^[26] and possess Sn-O distances of 2.775 Å and 2.729 Å, in line with other five-coordinate Sn species which have a dative oxygen interaction.^[24]



Figure 2. ORTEP representation of one of the conformers of 3 found in the unit cell. Selected interatomic distances [Å] and angles [°]: Sn(1)-C(16) 2.136(3), Sn(1)-C(22) 2.137(3), Sn(1)-C(28) 2.131(3), Sn(1)-C(1) 2.147(3), C(28)-Sn(1)-C(16) 112.06(11), C(28)-Sn(1)-C(22) 107.98(11), C(16)-Sn(1)-C(22) 106.58(12), C(28)-Sn(1)-C(1)109.26(12), C(16)-Sn(1)-C(1) 108.00(12), C(22)-Sn(1)-C(1) 113.01(12).

10.1002/chem.201703453

WILEY-VCH

FULL PAPER



Figure 3. ORTEP representation of 4 found in the unit cell. Selected interatomic distances [Å] and angles $[^0]$: Sn(1)-C(16) 2.155(3), Sn(1)-C(22) 2.126(3), Sn(1)-C(1) 2.4099(8), Sn(1)-C(1) 2.137(3), C(22)-Sn(1)-C(1) 124.05(14), C(22)-Sn(1)-C(16) 111.35(12), C(1)-Sn(1)-C(16) 116.35(13), C(22)-Sn(1)-Cl(1) 102.43(8), C(1)-Sn(1)-Cl(1) 97.67(9), C(16)-Sn(1)-Cl(1) 98.71(9).



Figure 4. ORTEP representation of **5** found in the unit cell. Selected interatomic distances [Å] and angles [°]: Sn(1)-C(16) 2.109(3), Sn(1)-C(15) 2.120(3), Sn(1)-Cl(1) 2.3917(8), Sn(1)-Cl(2) 2.3469(7), C(15)-Sn(1)-Cl(1) 101.40(9), C(15)-Sn(1)-Cl(2) 106.93(9), C(16)-Sn(1)-Cl(2) 107.04(7), C(16)-Sn(1)-Cl(1) 101.48(7).

Metal-Free Dehydrocoupling of 6

Metal-free dehydrocoupling of **6** (Scheme 4) was observed over a 10 d timeframe. A C_6D_6 solution of **6** in a Teflon sealed NMR tube protected from ambient light sources was monitored initially by NMR (¹H and ¹¹⁹Sn) spectroscopy. Physical changes (colour change, trace precipitate formation <10%) were observed and these changes thus characterized (NMR). The transparent orange colour characteristic of 6 in C₆D₆ noticeably darkened, along with the deposition of precipitate from the solution, after 24 h. There was an evident decrease in the relative integration of the ¹¹⁹Sn NMR signal (i.e., the -215 ppm signal for 5) and a new resonance appeared at -196 ppm (for 7-i). This value is typical of mixed aryl/alkyl polystannanes containing a propyloxy linkage.^[12] After 5 days, the Sn-resonance at -215 ppm had completely vanished with only the resonance at -196 ppm remaining. After 6 days, the colour of the observed semi-solid material changed from a dark yellow-orange to a bright yellow colour (Figure S2). Examination by ¹¹⁹Sn NMR spectroscopy revealed that the -196 ppm (presumed) polymer resonance was also decreasing in intensity and another new resonance at -235 ppm (7-f) began to appear. ¹¹⁹Sn NMR monitoring from the 7th to 10th day showed a further decrease in the intensity of the former resonance and a continued growth of the latter. The identity and possible structure of the polymeric component displaying the higher field ¹¹⁹Sn resonance will be discussed in the next section (vide infra).

Homopolymerisation of 6 with catalytic amounts of RhCl(PPh₃)₃

The homopolymer 7-f was also prepared by the slow addition of 6 (over 15 min) to a stirring toluene solution containing 4 mol% of catalyst (RhCl(PPh₃)₃) at RT for 4 h (Scheme 4). After this time, the sample volume was reduced in vacuo and, using a double-tipped cannula syringe, the liquid was transferred into a 10-fold excess of cold hexanes where an orange-yellow coloured semi-solid thereafter precipitated. This presumed polymer was recovered in 77% yield by carefully decanting off the hexanes followed by drying (in *vacuo*). The polymer is readily soluble in C_6D_6 and a ¹¹⁹Sn NMR spectrum of this material revealed a chemical shift (-236 [± 1] ppm: Table 2), similar to the value observed in the final product of the metal-free dehydrocoupling reaction. Polymer 7-f possesses a T_g of 22°C, with no evidence of a melt transition. A GPC analysis indicated that a moderate molecular weight polymer was indeed present (Table 2).

FULL PAPER



Synthesis of random co-polymer 8a (4:1) and 8b (1:1) using catalytic amounts of RhCl(PPh₃)₃

Two random co-polymers 8a-b were also prepared (Scheme 5) by incorporating (n-Bu)₂SnH₂, at two different loadings (4:1 and 1:1), during the metal-catalysed polymerisation. This was intended to produce a material with a modified (improved) solubility profile. The polymerisations and polymer recovery were carried out under similar conditions used to prepare homopolymer 7. These polymers, also semi-solid in nature, were dried under reduced pressure and orange coloured gels were thus isolated (Figure S3). The soluble polymers were characterized by ¹H, ¹³C and ¹¹⁹Sn NMR, elemental analysis, and GPC (Table 2). Characteristic of these random copolymers are two distinct ¹¹⁹Sn resonances (-168 and -243 ppm) that have been assigned to the $-(n-Bu)_2Sn$ - and $-(Ph)Sn-(CH_2)_3-O-(C_6H_4N=NC_6H_5)$ segments, respectively.



Alternating polymerisation of 6 and (n-Bu)₂SnH₂

We have previously demonstrated the facile condensation polymerisation of diaryl- or dialkyl tin dihydrides with dialkyl tin diamides.^[27] This led to the first examples of alternating polystannanes. Such an alternating polymer, 9, consisting of a 1:1 ratio of azo-stannyl and dibutyltin units was constructed using this strategy. The polymerisation was carried out at 0°C for 4 h in Et₂O solution, as shown in Scheme 6. The purification and recovery was similar to that used for the other polymers in this study. After washing with several portions of cold hexanes and drying in vacuo, an orange coloured, low molecular weight semi-solid was recovered (53% yield). A noteworthy property of this material is that three resonances were detected in the ¹¹⁹Sn NMR spectrum (Table 2) indicating that two structural motifs may be present in the polymer backbone (vide infra).

Characterization and Potential Structures of Polymers 7, 8ab, 9

As noted above, ¹¹⁹Sn NMR resonances for the polymers (Table 2) indicate that at least two structural forms may be present due perhaps to variations in the structural backbone of such prepared under metal-free conditions. This characteristic is also observed for the alternating polymer. Polymers such as **10**, with similar flexible propyloxy ligands capable of datively bonding to Sn atoms, typically display ¹¹⁹Sn resonances between -190 and -197 ppm.^{[12],[21]} A plausible explanation for the observed spectroscopic behaviour herein is that there are datively bonded $(O \rightarrow Sn)$ and unbound propyloxy species along the polymer chain.





Further, exposure to ambient light sources, even for a short time, may also cause (E)/(Z)-isomerization in the azobenzene moiety, and the additional crowding of this organic fragment in the (Z)-conformer could facilitate its release from dative interactions. Alternatively, dative interactions may also include lone pair electrons found on the -N=N- unit of the azobenzene. In cases where small molecule stannanes are found in tetrahedral environments by X-ray crystallography, such as in 3, an upfield chemical shift (-100 ppm) is typically observed.^[12] Similarly, it is expected that species such as dihydride 6 likely adopt a similar distorted tetrahedral geometry because of the

10.1002/chem.201703453

WILEY-VCH

FULL PAPER

electronic environment at Sn; this is assumed to be more Lewis basic due to the attached hydrides. Resonances signals for this class of Sn atoms are also found upfield.^[28] These factors lead one to the suggestion that the non-metal catalysed route to the initially observed homopolymer 7-i forms in a presumed kinetically unstable conformation. This may be due to interactions such as those described above along the polymer backbone. Over time in solution, these fragments could re-organise to give a thermodynamically more stable end-product 7-f. In a constrained system, such as a highly substituted polystannane, it is logical to hypothesise that this process could be kinetically slow as observed. The metal-catalysed route to 7 appears to predispose these polymer groups to give 7-f directly: as observed by ¹¹⁹Sn NMR spectroscopy. A plausible explanation for this is that the Rh-bound stannyl groups are required to arrange themselves into a preferred conformation before the next Sn-Sn bond can be formed during polymerisation. For random co-polymers 8a, 8b and the alternating polymer 9, the downfield signal at δ = -167 ppm most likely represents the $-(n-Bu)_2Sn$ - unit and the resonances at δ = -243 ppm the azo-stannyl building block. For 9, the alternating polymer presents three ¹¹⁹Sn NMR resonances (Table 2) when the polymerisation was carried out by adding the diamide-tin to 6. The ¹¹⁹Sn NMR resonances for 9 therefore suggest that there may be both coordinated and free propyloxy units (Figure 5: vide supra).

Table 2. Characterization data for 7, 8a, 8b, 9 and 10.

Polymer	¹¹⁹ Sn NMR ppm (C ₆ D ₆)	M _w (Da) × 10⁴	Ð	Tg (°C)
7-i, 7-f No Cat.	-196, -235	-	1	
7-f Cat.	-236	2.85	1.1	22.0
8a (4:1)	-168, -243	3.53	2.4	N/A
8b (1:1)	-167, -241	1 st 7.80 2 nd 2.84	4.1 2.0	N/A
9	-167, -197, -240	1 st 1.60 2 nd 1.22	2.1 2.0	N/A
10 ^[21]	-195	2.45	1.8	64

The GPC and DSC data are also provided in Table 2. Only homo-polymer **7** possessed a detectable T_g value, lower than that observed for polystannanes such as **10**. The GPC chromatograms for all four new polymers in this study are shown in Figure 6. All polymers were bimodal and of moderate molecular weight. The corresponding values of the lower M_w fractions for **7** and **8b** could not be determined.





Figure 5. Bound and unbound polystannanes.



Computational studies

DFT calculations of **3-6** were carried out to gain insight into substituent and solvation effects on hypercoordinate bonding at the Sn centre. B3LYP geometry optimizations of **3-5** using the crystallographic molecular structures as initial guesses converged to equivalent conformations, with structural parameters in reasonable agreement with experiment. The calculated Sn-O separation distances were larger in each case (e.g. for **5**, Sn-O was 3.04 Å (calc.) as compared to 2.73 Å (expt.)), but reproduced the trend in diminishing Sn-O separation distance observed in **3-5**, as well as other structural differences.

The flexible propyloxy linkage between Sn and the azobenzene chromophore allows more than 30 possible conformations for each compound. A complete determination of the extent of hypercoordination for each compound would require a comprehensive conformational search followed by geometry optimization, frequency calculations and Boltzmann weighting for each conformer and then partitioning into fractions of hypercoordinated and non-hypercoordinated conformers. Examining the effect of solvation would necessitate repeating these calculations for each solvent considered. For the sake of expediency, we adopted the simpler approach of comparing the properties of two extremes: the fully extended conformer in which the propyloxy linkage has a trans-planar geometry (the "open"

FULL PAPER

conformer) and the conformer in which the linkage O atom most closely approaches the Sn atom (the "closed" conformer), as shown for **5** in Figure 7. These correspond, respectively, to the longest and shortest Sn-O separation distances within the set of conformers for each compound. In the absence of any stabilizing interaction between the Sn and O atoms, the open conformer should be the lowest energy conformer, since torsional strains and van der Waals repulsions are minimized. The closed conformer has substantial torsional strain due to the ring-like structure involving the propyloxy linkage and Sn.



Figure 7. Two conformational extremes for 5, (H atoms omitted for clarity) optimized structures (B3LYP/6-31(d,p):H,C,O,N,Cl; LANL08d:Sn).

Summed electronic and thermal free energies were determined for both conformers for each compound in the gas phase and in benzene and chloroform solvents using the Polarizable Continuum Model (PCM).^[29] The gas phase calculations (Table 3) show the effect of substitution on the Sn centre on the relative stabilities of the open and closed conformers: as phenyl substituents are replaced with chloro ligands in the series 3-5, the closed form becomes increasingly stable. This is consistent with greater Lewis acidity at the Sn centre resulting from substitution with the more electronegative chloro substituent. Like 3, the dihydride compound 6 has a large gas-phase calculated free energy difference between the open and closed conformers, with the open conformer significantly more stable, and the closed conformer calculated to make only a very small contribution to Boltzmann weighted average properties.

The calculations indicate that solvation significantly alters the relative stability of the open and closed conformers and that the magnitude of the effect varies by compound. In the case of **3**, the open conformer becomes substantially more stable in C_6H_6 and CHCl₃, while for **5**, the opposite is observed. The largest predicted changes in relative stability are observed for the dihydride **6**, with the closed conformer strongly disfavoured in the gas phase but roughly comparable in stability in C_6H_6 or CHCl₃ solution. The differences in solvation behaviour likely arise from variations in molecular charge distribution in open and closed conformers as well as between compounds. The significantly different dipole moments calculated for the compounds and conformations studied are consistent with this.

Table 3. B3LYP	Calculated	Relative	Free	Energies	for 3-6

Compound	Solvent	G _{open} − G _{closed} (kJ mol ⁻¹)	Boltzmann weight of closed conformer relative to open conformer at 298K
	-	-8.2	0.038
3	C ₆ H ₆	-12.3	0.0073
	CHCl₃	-15.8	0.0017
		-1.3	0.59
4	C ₆ H ₆	-4.3	0.17
	CHCl₃	-1.5	0.55
		-0.82	0.72
5	C ₆ H ₆	1.33	1.7
	CHCl₃	3.02	3.4
	_	-9.3	0.024
6	C ₆ H ₆	-1.4	0.56
	CHCl₃	1.3	1.7

As a rough first approximation to modelling hypercoordination in the polymer **7**, we calculated the relative free energies (B3LYP) for open and closed conformations of a Sn trimer: Me₃Sn-Sn(Ph)(-(CH₂)₃-O-(C₆H₄N=NC₆H₅)-SnMe₃. In the gas phase, *G*_{open} - *G*_{closed} is -8.0 kJ mol⁻¹, while in C₆H₆ solution the difference is -10.1 kJ mol⁻¹. These results suggest that conformers exhibiting hypercoordination may not predominate in C₆H₆ solutions of the hypothetical Sn trimer. The extent to which a simple trimeric model is an adequate representation for **7** may be questioned; the development of more sophisticated computational models for Sn polymers is currently in progress. The above result is best viewed as a benchmark for such hypercoordination phenomena in oligostannane models.

UV-Vis spectroscopy and Polymer stability

UV-Vis spectroscopy of all the azo-containing tin compounds (5-9) were performed using benzene solutions of the materials. Unsurprisingly, all compounds showed nearly identical absorption characteristics assigned to azo-containing units presumably absorbing energy to initiate (E)/(Z) transformations in solution. More intense absorbances were observed for all polymers in comparison with the monomeric species. Five consecutive scans of the all azo-containing tin polymers showed no evidence of degradation or photoscission when left in solution.

FULL PAPER





Further evidence of the stability of the azo-containing polymers was observed for a 100 mg sample of solid 7-f which was left exposed to moist air and sunlight for extended intervals. After 6 months, the colour of the semi-solid darkened from a light orange-colour to a somewhat darker shade of orange. However, there was no observable change in the solubility properties of this material nor the NMR (¹¹⁹Sn) resonances (-236 ppm only). This suggests long term stability with only the outer surface of this solid material being adversely affected. By comparison, when the gel-like orange coloured polymers 8a, 8b and 9 were left inside an open amber vial for slightly over one month, they transformed to insoluble darker brown coloured semi-solids which could not be further characterized. UV-Vis characterization of solutions of polymers 8b and 9 (C₆D₆) exposed to daylight, but sealed from moisture, displayed a decrease in signal intensity (57% and 23%, respectively) over a 120 day period, whereas 7-f was unchanged over the same time period (see Figure 8). The decrease in absorption intensity for 8b and 9 is likely due to the cleavage of Sn-Sn bonds (σ - σ * transitions masked by azo absorptions at 350-450 nm), while the azo Z- to Eabsorption contributions are presumably consistent. While the two copolymers are comprised of a similar number of stannylazo and dibutylstannyl units, the presumably more random polymeric structure appears to be more susceptible to chain cleavage. In contrast, 7f remains essentially stable under these conditions.

Conclusions

A six-step synthesis was carried out to prepare a polymerisable azo-containing tin dihydride monomer **6**. The first azo-containing tin homopolymer **7**, copolymers **8a** and **8b** and alternating polymer **9** were prepared. Polymer **7** gave strong evidence of being stable to both moist air and visible light, while polymers **8a**, **8b** and **9** became insoluble and thus likely slowly degraded under similar conditions. The azo-benzene functionality appears to provide unprecedented light stability to homopolystannanes and, in the case of **7**, provides the first evidence that a flexible, bulky, possibly coordinated unit is capable of providing a level of moisture and oxidation resistance to polystannanes. This investigation

also provides information as to the likely stability profile of polystannanes which contain Sn atoms devoid of such protecting groups (*i.e.*, the $-R_2Sn$ - units). Neighbouring azobenzene fragments do not appear to impart stability over the global polymer network. This suggests that the future design of mixed-polystannane polymers should incorporate monomers that are rich in protective functionalities such as light absorbing groups and fragments with chelation potential. Such concepts are currently being explored by us.

Experimental Section

Electronic Supplementary Information (ESI) available: Crystallographic data for compounds **3** (CCDC1549269), **4** (CCDC 1550051), and **5** (1549271) have been deposited with the Cambridge Crystallographic Data Centre. See DOI: 10.1039/b000000x/

All synthetic details and experimental results are provided in the ESI.

Acknowledgements

This work is supported by the NSERC Discovery program. The computational studies were made possible by the facilities of the Shared Hierarchical Academic Research Computing Network (SHARCNET:www.sharcnet.ca) and Compute/Calcul Canada.

Keywords: Polystannanes, Azobenzenes, hypercoordination

- T. S. Arrhenius, M. Blanchard-Desce, M. Dvolaitzky, J.-M. Lehn, J. Malthete, *Proc. Natl. Acad. Sci.* **1986**, *83*, 5355– 5359.
- F. C. Grozema, L. D. A. Siebbeles, in *Charg. Excit. Transp.* through Mol. Wires (Eds.: F.C. Grozema, L.D.A. Siebbeles), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2011, pp. 1–16.
- [3] W. Y. Lo, N. Zhang, Z. Cai, L. Li, L. Yu, Acc. Chem. Res.
 2016, 49, 1852–1863.
- [4] R. West, J. Organomet. Chem. 1986, 300, 327–346.
- [5] R. D. Miller, J. Michl, Chem. Rev. 1989, 89, 1359–1410.
- [6] C. S. Weinert, in *Comphrensive Organomet. Chem. III* (Eds.: D.M. Mingos, R.H. Crabtree), Elsevier, Amsterdam, 2007, pp. 699–808.
- [7] T. Imori, T. D. Tilley, J. Chem. Soc. Chem. Commun. 1993, 1607–1609.

Chemistry - A European Journal

10.1002/chem.201703453

WILEY-VCH

FULL PAPER

- [8] V. Lu, T. D. Tilley, *Macromolecules* **1996**, *29*, 5763–5764.
- [9] F. Choffat, P. Smith, W. Caseri, J. Mater. Chem. 2005, 15, 1789–1792.
- [10] F. Choffat, P. Wolfer, P. Smith, W. Caseri, *Macromol. Mater. Eng.* 2010, 295, 210–221.
- [11] F. Choffat, P. Smith, W. Caseri, Adv. Mater. 2008, 20, 2225–2229.
- [12] A. Khan, A. Patel, S. Komejan, C. Lombardi, A. J. Lough,
 D. A. Foucher, J. Organomet. Chem. 2014, 776, 180–191.
- [13] A. Natansohn, P. Rochon, *Chem. Rev.* 2002, 102, 4139–4175.
- [14] D. Hagberg, Synthesis of Organic Chromophores for Dye Sensitized Solar Cells, PhD. Thesis, KTH Chemical Science and Engineering, 2009.
- [15] E. Merino, Chem. Soc. Rev. 2011, 40, 3835–3853.
- [16] J. Christoffers, T. Werner, A. Baro, P. Fischer, J. Organomet. Chem. 2004, 689, 3550–3555.
- [17] Z. Mahimwalla, K. G. Yager, J. I. Mamiya, A. Shishido, A.
 Priimagi, C. J. Barrett, *Polym. Bull.* 2012, *69*, 967–1006.
- [18] E. Merino, M. Ribagorda, *Beilstein J. Org. Chem.* 2012, *8*, 1071–1090.
- [19] J. L. Wardell, J. M. Wigzeli, J. Chem. Soc., Dalton. Trans. 1982, 2321–2326.
- [20] Yoshihiro Yoshida, Yoshiko Sakakura, N. Aso, Shin Okada,

Y. Tanabe, Tetrahedron 1999, 55, 2183-2192.

- [21] P. R. Deacon, N. Devylder, M. S. Hill, M. F. Mahon, K. C. Molloy, G. J. Price, *J. Organomet. Chem.* **2003**, *687*, 46– 56.
- [22] T. Munguia, I. S. Pavel, R. N. Kapoor, F. Cervantes-Lee, L. Párkányi, K. H. Pannell, *Can. J. Chem.* **2003**, *81*, 1388– 1397.
- [23] T. Imori, V. Lu, H. Cai, T. D. Tilley, J. Am. Chem. Soc.
 1995, 117, 9931–9940.
- [24] A. Khan, D. A. Foucher, Coord. Chem. Rev. 2015, 312, 41– 66.
- [25] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* 2007, 955–964.
- [26] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton. Trans.* **1984**, 1349– 1356.
- [27] S. Harrypersad, D. Foucher, *Chem. Commun.* **2015**, *51*, 7120–7123.
- [28] V. Y. Lu, T. D. Tilley, *Macromolecules* **2000**, 33, 2403– 2412.
- [29] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999–3093.

FULL PAPER

Layout 1:

FULL PAPER

Polystannanes with azobenzene ligands demonstrate improved moisture and light stability



Jeffrey Pau, Alan J. Lough, R. Stephen Wylie, Robert A. Gossage, and Daniel A. Foucher*

Page 1 – Page 9

Proof of Concept Studies Directed Towards Designed Molecular Wires: Property Driven Synthesis of Air and Moisture-Stable Polystannanes