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Introduction

Polystannanes are unique conductive main group polymers comprised entirely of a backbone of tin atoms.¹ While generally more stable in their solid form, in solution these soluble, film forming materials² display an extreme sensitivity to light and moisture and hence readily depolymerize to yield cyclic stannanes.³ Our interest in these polymers is focused on the tailoring of such polystannanes to improve their stability and also to explore their utility as conductive, one-dimensional polymeric wires.⁴ We are currently investigating strategies towards more stable polystannanes including the attachment of light absorbing groups⁵ (e.g. ultra violet absorbers, UVA's) to the tin centers to protect sensitive Sn-Sn bonds, the preparation of 5- and 6-coordinate tin centers that moderate the Lewis acidic nature of Sn(IV)^{6,7} and the chemistry of alkyne insertion into the weak Sn-Sn backbones of polystannanes to produce potentially stable polycarbostannanes, a new class of Group 14 conjugated polymers. The work reported herein deals with this latter approach.

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Pd-catalysed reactions of alkynes with model distannanes and poly[di-(*n*-butyl)]stannane†

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A reinvestigation of Pd-catalysed alkyne (R'–C=CH; R' = H, Ph) insertion chemistry involving R₃SnSnR₃ (**3a**: R = Me; **3b**: R = *n*-Bu) was undertaken. Model distannyl ethylenes **4a–b** (Me₃SnCH=CR'SnMe₃) and **5a–b** ((*n*-Bu)₃SnCH=CR'Sn(*n*-Bu)₃) were reproduced and further characterized by NMR (¹¹⁹Sn, ¹³C, ¹H) and UV-Vis spectroscopy. In the presence of an excess of phenylacetylene, dimerization–carbostannylation of compound **4b** yielded the new conjugated butadiene, (*Z*,*Z*)-1,4-bis(trimethylstannyl)-1,4-diphenyl-buta-1,3-diene (**9**). An X-ray structure determination of **9** reveals a symmetrical double-bond *Z* confirmation. Compound **9** was further characterized by NMR, UV-Vis spectroscopy, and MS. A DFT analysis of model compounds (**4a–b**, **5a–b**, **9**) and the experimental and theoretical λ_{max} values from the UV-Vis spectra were also compared. Acetylene and phenylacetylene Pd-catalysed insertion into the backbone of poly[di-(*n*-butyl)] stannane **12** resulted in new, modest molecular weight, partially inserted alkene tin polymers (**13a–b**) that were also characterized by GPC, NMR, UV-Vis spectroscopy and elemental analysis.

Metal-catalysed insertion of alkynes into Group 14 disilanes⁸ and digermanes⁹ (Fig. 1) was successfully demonstrated by Tanaka *et al.* In these reactions, Pd-catalysed insertion of alkynes into Si or Ge dimers or trimers (C₆H₆; 120 °C: sealed tube) leads to formation of disilalkenes (1), digermalkenes or trigermadialkene (2) derivatives. Metal-catalysed alkyne insertion into hexalkyldistannanes (3) was first attempted in the early 1970s.¹⁰ Using Pd(PPh₃)₄ as catalyst (neat; 50–85 °C), Mitchell was able to prepare more than 20 varieties of distannylalkenes (4, 5) from the addition of alkynes to distannanes.¹¹ Characteristic of many of these distannylalkenes is the facile photoinduced transformation from *Z* to *E* isomers when such molecules are irradiated with UV light. In the 1990s, Piers and Skerlij investigated the Pd-

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Fig. 1 Group 14 dimers and alkyne inserted dimers and trimers.

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catalysed insertion of alkynoates into distannanes and followed their thermal conversions from *Z* to *E* isomers.¹² Similar metal-catalysed insertions of alkynes into [2]ferrocenophanes with disilane¹³ or distannane¹⁴ (**6**) bridges (Fig. 2) were carried out independently in both the Manners and Heberhold laboratories, respectively. Alternative, non-catalysed routes to alkene (**5a**) and diene (7) materials of this type was previously demonstrated by Corey,¹⁵ Seitz¹⁶ and Ashe.¹⁷ The utility of these distannylalkenes species in both cross-coupling^{1*h*,18} chemistry and transmetallation¹⁹ strategies is well established.

The insertion chemistry of Group 14 polymers is not, however, extensively explored. The Pd-catalysed insertion of alkynes into the backbones of polysilanes, polycarbodisilanes and oligogermanes was demonstrated in work largely carried out by both Tanaka²⁰ and Mochida.⁹ This insertion chemistry rarely goes to completion and therefore results in random block copolymers with repeating units that contain both alkene units between two of the Group 14 elements and those in which the Si-Si⁸ or Ge-Ge⁹ bonds remain undisturbed. The electrochemical and spectroscopic properties of these alkyne inserted systems have also not been extensively investigated. Tanaka reported that the UV-Vis spectra of partially (80%) alkyne inserted polycarbosilanes (8) showed nearly identical $\lambda_{\rm max}$ values to that of the parent polymer but doped conductivity values $(3-10 \times 10^{-4} \text{ S cm}^{-1})$ that are far superior to the unmodified polymer.²⁰ As polysilanes inherently behave as positive photoresists,²¹ the potential to enhance the light stability of these polymers is desirable. Unfortunately, the improvement of the light stability following insertion within this system was not mentioned.²⁰

We describe herein our efforts to re-investigate the Pd-catalysed alkyne insertion reactions of distannanes and provide further characterization of the resulting products by NMR (¹¹⁹Sn, ¹H, ¹³C) and UV-Vis spectroscopies. Gas phase structures of model compounds (**4a–b**, **5a–b**) and novel compound **9** were examined by density functional theory (DFT) at the B3LYP 6-31G* level. Additionally, we report on our attempts to insert acetylene and phenylacetylene into the backbone of a light sensitive poly[di-(butyl)]stannane (**12**) and detail the impact of this chemistry on the light stability of the resulting polycarbostannanes (13a, 13b).

Results and discussion

SnMe₃

Me

Pd-catalysed alkyne insertion into distannanes and X-ray structure of 9

The Pd-catalysed insertion reactions of alkynes into hexalkyldistannanes was first reported by Notles¹⁰ and later by Mitchell.^{11a-d} These reactions proceed via cis-addition of the alkyne into the Sn-Sn bond, which will then readily convert to the more stable trans product upon exposure to light. In particular, insertion of acetylene or phenylacetylene with 3a (R = Me) proceed to near completion (4a and 4b); in contrast incomplete addition is observed in the case of 3b (R = *n*-Bu) yielding the products 5a or 5b. As shown in Scheme 1 for 4b, the reactions likely proceed through an initial oxidative-addition of the distannane by Pd, followed by insertion of the alkyne, resulting in the cis-Pd intermediate and reductive elimination of the product that generates the distannylalkene 4b. Characterization data (NMR: ¹¹⁹Sn, ¹H, ¹³C; C₆D₆) for both **4a** and **4b** agreed with the reported chemical shifts and coupling constants for these products.^{11b} Insertion of acetylene into 3b was reported by Mitchell,^{11b} but no characterization data for the product **5a** was provided. Compound 5a has previously been prepared by noninsertion routes¹⁵ and the reported chemical shift data (¹H NMR) is in good agreement with this work. The related Pd-catalysed insertion of phenylacetylene into 3b leads to the previously prepared, but uncharacterized, distannylalkene 5b.

In the presence of an excess of phenylacetylene (>2.0 equiv.), we have observed the formal insertion of one additional unit of phenylacetylene (presumably by *cis* insertion) into the *cis*-Pd intermediate $(Me_3Sn)(PPh_3)_2Pd-CH=C(Ph)(SnMe_3)$, which leads to the photochemically and



Scheme 1 Proposed reaction pathway for the formation of 4b and 9.

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thermally stable (*Z*,*Z*)-1,4-bis(trimethylstannyl)-1,4-diphenylbuta-1,3-diene (9). A single δ_{119Sn} resonance at -44 ppm was observed for 9.

We propose that a second phenylacetylene insertion between the remaining Sn-Pd bond (see Scheme 1) occurs, followed by reductive elimination and a concomitant C-C bond forming step leading to 9. This process is similar to the dimerization-carbostannylation products first reported by Tsuji et al.²² (10) and later by Hiyama and co-workers (11).²³ As with 9, compounds 10 and 11 (Fig. 3) are very likely the result of regio- and stereo-selective reactions to yield the (E,E)-1,4 adduct and the (E,E)-conjugated $\alpha,-\omega$ pentacenes, respectively. Surprisingly, despite an excess of acetylene, a similar reaction is not observed in the case of acetylene insertion with 3a. This may be the result of the difference in reaction conditions (i.e., bubbling acetylene in to dioxane together with 3a, rather than the neat reaction of phenylacetylene with 3a). The formation of the 2:1 insertion product 9 may be thermodynamically favoured, and will only occur in the presence of an additional equivalent of phenylacetylene.

Compound **9** was further examined in the solid-state by single crystal X-ray diffraction (Fig. 4; Table 1). The crystallographic data of **9** confirm that a second phenylacetylene unit has inserted in a head-to-head fashion, with the molecule crystallizing in the double *Z* conformation. The lengths of the single and double bonds of **9** are inequivalent at 1.445 and 1.355 Å, a situation that has been previously observed in the repeat unit of the backbone in *t*-butyl terminated *trans*-dodecahexaene²⁴ (avg. values 1.44 and 1.34 Å, respectively).

UV-Vis and DFT analysis of distannylethylenes

Solution UV-Vis spectroscopy (THF) of compounds **3a**, **4b** and **9** (Table 2) show a noticeable redshift in the observed λ_{max} following alkyne insertion. This is consistent with the structure of **9** as a model for a conjugated polyene.²⁶ A DFT analysis (B3LYP 6-31G* level) of stannanes and distannylalkenes (**4a**, **4b**, **5a**, **5b**) and the distannyldiene (**9**) were also undertaken to investigate the impact of introducing π -bridging units into the Sn–Sn σ -bond. Calculated λ_{max} values for these compounds (Table 2) agree well with the experimental data and suggest that insertion of the phenylacetylene into a Sn–Sn bond leads



Fig. 4 ORTEP representation of a molecule of **9** with thermal ellipsoids drawn at the 30% probability level. Selected bond lengths (Å) and angles (°). Sn(1)–C(4) 2.189(13), Sn(2)–C(1) 2.148(14), C(1)–C(2) 1.37(2), C(1)–C(5) 1.481(19), C(2)–C(3) 1.445(18), C(3)–C(4) 1.343(19),C(4)–C(11) 1.501(18), C(3)–C(4)–Sn(1) 120.4(10), C(1)–C(2)–C(3) 125.2(12), C(4)–C(3)–C(2) 128.0(12).

Table 1 Crystal data and structure refinement for 9

Empirical formula	$C_{22}H_{30}Sn_2$
Formula weight	531.84
Crystal colour	Yellow
$T(\mathbf{K})$	150(1)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pca21
<i>a</i> (Å)	16.1862(3)
$b(\mathbf{A})$	6.2126(6) Å
<i>c</i> (Å)	22.2214(11) Å
α (°)	90
β (°)	90
γ (°)	90
Volume (Å ³)	2234.5(2)
Z	4
$D_{\text{calc}} (\text{Mg m}^{-3})$	1.581
Absorption coefficient (mm^{-1})	2.236
F(000)	1048
Crystal size (mm ³)	0.16 imes 0.10 imes 0.10
θ range (°)	2.68 to 27.46.
Index ranges	$-20 \le h \le 21, -8 \le k \le 8,$
	$-22 \le l \le 28$
Reflections collected	13 220
Independent reflections	$4024 \left[R_{\text{int}} = 0.0906 \right]$
Completeness to θ (%)	99.3% (θ = 27.46°)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.767 and 0.658
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4024/1/222
Goodness-of-fit on F^2	1.036
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0590, wR_2 = 0.1328$
<i>R</i> indices (all data)	$R_1 = 0.1033, wR_2 = 0.1620$
Absolute structure parameter	0.58(9)
Largest diff. peak and hole (e $Å^{-3}$)	2.028 and -1.675

to a destabilization of the HOMO and stabilization of the LUMO orbitals (**3a**: $\Delta E_{\text{HOMO-LUMO}} = 6.66$ eV *vs.* **9**: 4.07 eV), resulting in a redshift. This is consistent with a conjugated σ - π overlap. The frontier orbitals suggest that this σ - π overlap is unhindred by the nodes centered on the p orbitals. A comparison of selected bond lengths and bond angles of **9** as

Table 2 ¹¹⁹Sn NMR (C₆D₆) chemical shifts and experimental (THF) and calculated UV-Vis λ_{max} values of distannanes (**3a** and **3b**) and model distannylalkenes (**4a**, **4b**, **5a**, **5b** and **9**)

Compound	δ^{119} Sn (ppm)	Calc. (λ_{\max}) nm	Exp. (λ_{\max}) nm, $(\varepsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1})$
3a	-109	206	210^a
3b	-83	214	245^{b} , (75 930)
4a	[E, -54.7, Z, -61.4]	197	237^{b} , (67 200)
4b	[E, -45.7, -59.6, Z]	223	234^{b} , (26 250)
	-39.0, -62.0]		
5a	-68.3	216	244^{b} , (81 400)
5b	[E, -54.7, -66.5, Z,	223	235 ^b
	-53.5, -66.1]		
7	[Z, -53.6, E, -35.2]	236	249^{c}
9	-44.0	312	309^{b} , (1400)
a			

^{*a*} Ref. 25. ^{*b*} This work. ^{*c*} Ref. 17.



Scheme 2 Insertion of acetylene and phenylacetylene in to the backbone of poly[di-(butyl)]stannane (12) to produce the copolymer (13a) and the random copolymer (13b).

measured (X-ray) and calculated by DFT are given in the ESI:^{\dagger} Table S-1.^{\ddagger}

Pd-catalysed insertion of alkynes into polystannane 12

Insertion reactions of alkynes into polystannane 12 (Scheme 2) were also attempted. Using conditions similar to those for the insertion of alkynes into distannanes, two new polymers 13a and 13b were produced. Pd-catalysed insertion of acetylene into 12 (1,4-dioxane) yields (4d: 85 °C) an orange-coloured, presumably polymeric, product (13a). Analysis of the crude material by NMR (¹¹⁹Sn) shows at least five new resonances but no evidence for 12. Precipitation into cold methanol and recovery reveals (NMR) a single δ_{119Sn} resonance (-66.5 ppm), in a similar chemical shift range for that of 3b inserted with acetylene (5a). ¹H NMR of 13a suggests that the insertion proceeds to approximately 50% of the Sn-Sn bonds, leaving on average all of the Sn centers with a single acetylene carbon bond and one Sn-Sn bond. Elemental analysis of 13a supports the proposed structure shown in Scheme 2. This polymer appears to be indefinitely stable to ambient light and was isolated as an orange powder. GPC analysis (Table 3) shows evidence of some depolymerization, with a significant weight loss (\approx 45%) from the parent polymer **12**.

Table 3 ¹¹⁹Sn (C₆D₆) chemical shifts, molecular weight data and experimental UV-Vis (THF) λ_{max} values of polystannane **12** and polycarbostannanes **13a** and **13b**

Compound	δ^{119} Sn (ppm)	$M_{ m w}$ (abs), PDI	Exp. (λ_{\max}) nm, $(\varepsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1})$
12 13a	-190 -66.5	1.2×10^4 , 1.6 5.3×10^3 , 1.8	380, (760) 320, (80)
13b	-66.1, -190.6	1.3×10^4 , 1.5	370, (970)



Fig. 5 Comparison of UV-Visible spectra (THF) of alkyne inserted and non-inserted tin products.

Attempts to insert phenylacetylene into **12** under reaction conditions similar to the synthesis of **13a** were unsuccessful. Insertion was carried out from the neat reaction of **12** with phenylacetylene in the presence of Pd catalyst at elevated temperatures (5d: 85 °C). Analysis by GPC revealed the resultant polymer (**13b**) to be of a slightly higher molecular weight (Table 3), indicative of the insertion of the phenylacetylene. Analysis (NMR) showed two δ_{119Sn} resonances at -66.1 and -190.6 ppm suggestive of a more random structure. The resonance at -190.6 ppm, which is similar to the parent polymer **12**, indicates that there is likely only a partial substitution of the backbone.

UV-Vis analysis of the new polycarbostannanes **13a** and **13b** in THF show λ_{max} absorbances that extend into the visible, but are slightly blue shifted from the parent polystannane **12** (Table 3, Fig. 5).

Similar to the properties reported by Tanaka and coworkers⁸ for the polycarbosilane **8**, insertion into Sn–Sn bonds by alkynes does not seem to disrupt conjugation in the molecular backbone. The UV stability of **13a** and **13b** was evaluated by multiple (>50) UV-Vis scans over a **1** h time period. Both **13a** and **13b** show remarkable stability, with virtually no change in their UV-Vis characteristics compared to the parent polymer **12**, which completely decomposes after only ten consecutive scans.

Conclusion

We have carried out a reinvestigation of the Pd-catalysed insertion chemistry of acetylene and phenylacetylene into distannanes (**3a**, **3b**) to yield the mono-inserted products **4a**, **4b**, **5a** and **5b**. In the case of **3a**, reaction with excess phenylacetylene

 $[\]ddagger Resolution of {\rm ^{119}Sn^{-13}C}$ and ${\rm ^{117}Sn^{-13}C}$ couplings in some instances could not be made.

results in an unusual dimerization–carbostannylation (*vide supra*) product **9**. An X-ray analysis of **9** reveals a head-to-head arrangement of phenylacetylene units. Pd-catalysed alkyne insertions into polystannane **12** results in new, modest molecular weight polycarbostannanes **13a** and **13b** which show improved light stability relative to the parent polymer. Further investigations into polymeric materials of this type are ongoing.

Experimental

General procedures

All manipulations of air and/or moisture-sensitive compounds were performed under $N_2(g)$ atmosphere in a glovebox or using standard Schlenk techniques. Me₆Sn₂ (3a) and (n- $Bu_{6}Sn_{2}$ (3b) were purchased from Strem and used as received. $(n-Bu)_2SnH_2$ used to prepare the polystannane $[(n-Bu)_2Sn]_n$ (12) was prepared from (n-Bu)₂SnCl₂ and LiAlH₄ according to a literature preparation.^{1b,2a} Solvents were dried by standard procedures prior to use. ¹H, ¹³C{¹H} and ¹¹⁹Sn{¹H} NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer. ¹H spectra were referenced to the residual solvent peaks in the deuterated solvents (in turn referenced to external TMS) while the ¹³C spectra are referenced internally to the deuterated solvent resonances which are also in turn referenced to TMS (δ = 0.00 ppm). ¹¹⁹Sn resonances were referenced to external SnMe₄ (δ = 0.00 ppm). UV-Vis measurements were carried out in THF solutions using a Perkin Elmer Lamda 40 spectrometer. 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 (λ_0 = 670 nm) and a low angle (7°) 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 the eluent. GPC samples were prepared using 3-10 mg of polymers per mL THF, and filtered using a 0.45 µm filter. High resolution mass spectrometry experiments were carried out using an accuTOF DART-MS at the University of Toronto. Elemental analyses were performed by Atlantic Microlab of Norcross Georgia. The gas phase molecular calculations (DFT) of model compounds (4a-b, 5a-b) and novel compound 9 were performed by using Spartan 10.0 V1.1.0 software program at the B3LYP 6-31G* level.

Insertion of alkynes into Sn-Sn bonds

Compounds 4a, 4b, 5a, and 5b were prepared according to the method previously described by Mitchell *et al.*^{11b}

COMPOUND 4A: REACTION OF 3A WITH ACETYLENE. The distannane 3a (1.05 g, 3.2 mmol) and Pd(PPh₃)₄ (10 mg, 8.6×10^{-3} mmol) were weighed and transferred to a reaction flask in a glove box. The reaction mixture was then diluted with 20 mL of 1,4-dioxane, warmed to 60 °C, and acetylene gas was thereafter bubbled into the flask for 4 h. The contents of the flask turned

brown in colour during this time period. The solvent was then removed under reduced pressure and the product **4a** recovered as a red brown semi-solid. The NMR (¹¹⁹Sn, ¹³C, and ¹H) data in C_6D_6 was in good agreement for the exclusive initial formation of the *Z* isomer with the data reported by Mitchell *et al.*^{11b} and provided here for completeness. Yield = 0.96 g (85%).

¹H NMR (C₆D₆) δ (ppm): 0.28 (s, 18H, ²J_{119Sn-H} (Sn-CH₃) = 53.98 Hz, ²J_{117Sn-H} (Sn-CH₃) = 52.74 Hz), 7.39 (s, 2H, ³J_{HH} (=CH) = 17.1 Hz, ²J_{119Sn-H} (=CH-Sn) = 102.4 Hz, ²J_{117Sn-H} (=CH-Sn) = 97.60 Hz, ³J_{119Sn-H} (CH=CH-Sn) = 216.6 Hz, ³J_{117Sn-H} (CH=CH-Sn) = 207.6 Hz), ¹³C{¹H} NMR (C₆D₆) δ (ppm): -8.8 (s, -Sn-CH₃), 154.7 (s,=CH-Sn), ¹¹⁹Sn{¹H} NMR (C₆D₆) δ (ppm): -61.37 (J_{119Sn-117Sn} = 470.2 Hz). UV-VIS: λ_{max} (THF)/nm 237 (ε /dm³ mol⁻¹ cm⁻¹ 67 200).

COMPOUND 5A: REACTION OF 3B WITH ACETYLENE. The distannane 3b (1.2 g, 2.06 mmol) and Pd(PPh₃)₄ (40 mg, 3.5×10^{-2} mmol) were added to a reaction flask in a glove box. The reaction mixture was diluted with 20 mL of 1,4-dioxane, warmed to 85 °C, and acetylene gas was thereafter bubbled into the flask for 100 h. The contents of the flask turned brown in colour during this period. The solvent was then removed under reduced pressure and the product 5a recovered as a moisture-sensitive, red coloured oil. Analysis of the crude reaction product by ¹¹⁹Sn NMR (C₆D₆) revealed only one signal for the acetylene inserted product 5a. Yield = 0.3 g (24%).

¹H NMR (C₆D₆) δ (ppm): 0.95 (t, 3H, ³J_{HH} = 14.6 Hz, CH₃CH₂CH₂CH₂-Sn), 1.07 (m, 2H, CH₃CH₂CH₂CH₂-Sn), 1.41 (m, 2H, CH₃CH₂CH₂CH₂-Sn), 1.64 (m, 2H, CH₃CH₂CH₂CH₂-Sn), 7.59 (s, 2H, ${}^{3}J_{HH}$ (=CH) = 17.7 Hz, ${}^{2}J_{119}_{Sn-H}$ (=CH-Sn) = 93.3 Hz, ${}^{2}J_{117Sn-H}$ (=CH-Sn) = 87.3 Hz, ${}^{3}J_{119Sn-H}$ (CH=CH-Sn) = 201 Hz, ${}^{3}J_{117Sn-H}$ (CH=CH-Sn) = 194 Hz), ${}^{13}C{}^{1}H$ NMR (C₆D₆) δ (ppm): 10.77 (¹ $J_{119Sn-C}$ (CH₃CH₂CH₂CH₂-Sn) = 330 Hz, ¹ $J_{117Sn-C}$ $(CH_3CH_2CH_2CH_2-Sn) = 315 Hz)$, 13.99 $(CH_3CH_2CH_2CH_2-Sn)$, 27.91 $({}^{3}J_{119Sn-C}$ (CH₃CH₂CH₂CH₂-Sn) = 56.0 Hz, ${}^{3}J_{117Sn-C}$ $(CH_3CH_2CH_2CH_2-Sn) = 55.0 Hz$, 29.75 $(^2J_{119Sn-C})$ $(CH_3CH_2CH_2CH_2-Sn) = 19.7 \text{ Hz}, {}^2J_{117}Sn-C} (CH_3CH_2CH_2CH_2-Sn)$ = 19.7 Hz), 154.24 (${}^{1}J_{{}^{119}Sn-C}$ (-Sn-CH==) = 428 Hz, ${}^{1}J_{{}^{117}Sn-C}$ (-Sn-CH=) = 410 Hz, ${}^{2}J_{119Sn-C}$ (-Sn-CH=) = 34.3 Hz, ${}^{2}J_{117Sn-C}$ (-Sn-CH= = 34.3 Hz), ¹¹⁹Sn{¹H} NMR (C₆D₆) δ (ppm): -68.3 $({}^{3}J_{{}^{119}\text{Sn}^{-117}\text{Sn}} = 342.0 \text{ Hz}).\ddagger \text{UV-VIS: } \lambda_{\text{max}}(\text{THF})/\text{nm} 244 (\epsilon/\text{dm}^{3})$ $mol^{-1} cm^{-1} 81 400$).

COMPOUND 4B: REACTION OF 3A WITH PHENYLACETYLENE. The distannane **3a** (1.55 g, 4.7 mmol), phenylacetylene (483 mg, 4.7 mmol) and Pd(PPh₃)₄ (10 mg, 8.6 × 10⁻³ mmol) were weighed into a reaction flask in a glove box. The neat reaction mixture was heated (80 °C) for 72 h. Analysis by ¹¹⁹Sn NMR (C₆D₆) initially revealed resonances for both the *cis* and *trans* isomers of **4b**, as previously reported,^{11b} with full conversion to the *trans* isomer of **4b** occurring under ambient light conditions in 1 week. Yield = 1.1 g (55%).

¹H NMR (C₆D₆) δ (ppm): 0.20 (s, 9H, ²J_{Sn-H} (Sn-CH₃) = 53.8 Hz), 0.23 (s, 9H, ³J_{Sn-H} (C₆H₅-C-Sn-CH₃) = 51.9 Hz), 7.03-7.18 (m, 5H, C₆H₅-), 6.92 [7.37] (br m, 1H,=CH), ¹³C{¹H} NMR (C₆D₆) δ (ppm): -7.39 [-7.42] (¹J_{119Sn-C} (HC-Sn-CH₃) = 333 Hz, ¹J_{117Sn-C} (HC-Sn-CH₃) = 319 Hz), -6.56 [-6.58] (¹J_{119Sn-C} (C₆H₅-

C–Sn–CH₃) = 343 Hz, ¹ $J_{117Sn-C}$ (C₆H₅–C–Sn–CH₃) = 328 Hz), 126.25 (*p*-C₆H₅), 128.52 (*m*-C₆H₅), 132.40 (*o*-C₆H₅), 148.9 (¹ $J_{119Sn-C}$ C₆H₅–C=CH–Sn = 491 Hz, ² $J_{119Sn-C}$ C₆H₅–C=CH–Sn = 69 Hz, ¹ $J_{117Sn-C}$ C₆H₅–C=CH–Sn = 468 Hz, ² $J_{117Sn-C}$ C₆H₅– C=CH–Sn = 66 Hz), 150.82 (¹ $J_{119Sn-C}$ i-C₆H₅–Sn = 98 Hz, ² $J_{119Sn-C}$ i-C₆H₅–Sn = 56 Hz, ¹ $J_{117Sn-C}$ i-C₆H₅–Sn = 94 Hz, ² $J_{117Sn-C}$ i-C₆H₅– Sn = 54 Hz), 169.0 (¹ $J_{119Sn-C}$ C₆H₅–C=CH–Sn = 497 Hz, ² $J_{119Sn-C}$ C₆H₅–C=CH–Sn = 40 Hz, ¹ $J_{117Sn-C}$ C₆H₅–C=CH–Sn = 456 Hz, ² $J_{117Sn-C}$ C₆H₅–C=CH–Sn = 40 Hz), ¹¹⁹Sn{¹H} NMR (C₆D₆) δ (ppm): -45.7 [–38.97], -59.62 [62.00].§ UV-VIS: λ_{max} (THF)/nm 234 (ε /dm³ mol⁻¹ cm⁻¹ 26 250).

COMPOUND 5B: REACTION OF 3B WITH PHENYLACETYLENE. The distannane **3b** (1.0 g, 3.0 mmol), phenylacetylene (352 mg, 3.4 mmol) and Pd(PPh₃)₄ (10 mg, 8.6 × 10⁻³ mmol) were weighed into a reaction flask in a glove box. The neat reaction mixture was heated (80 °C) for 72 h. Analysis by ¹¹⁹Sn NMR (C₆D₆) revealed resonances for the *cis* isomer along with a resonance at -83.6 ppm for the unreacted starting material (**3b**). The reaction proceed to only 35% conversion to **5b** as measured by ¹H NMR. No attempt to isolate the product was made. This was a similar result observed earlier by Mitchell *et al.* for this compound.^{11a}

 ^{1}H NMR (C_6D_6) δ (ppm): 0.92–1.7 (m, 54H, CH₃CH₂CH₂CH₂-Sn), 6.94 (br m, 1H,=CH), 7.00-7.52 (m, 5H, C_6H_5 -), ${}^{13}C_{1}^{1}H_{1}^{1}$ NMR (C_6D_6) δ (ppm): 10.29 (s, CH₃CH₂CH₂CH₂-Sn-CH=), 10.68 (s, CH₃CH₂CH₂CH₂-Sn-CPh=), 13.95 (CH₃CH₂CH₂CH₂-Sn-CH=), 13.98 (CH₃CH₂CH₂CH₂-Sn-CPh=), 27.67 (CH₃CH₂CH₂CH₂-Sn-CH=), 29.74 (CH₃CH₂CH₂CH₂-Sn-CPh=), 126.37 (*p*-C₆H₅), 128.45 (*m*-C₆H₅), 132.50 (*o*-C₆H₅), 148.0 (¹*J*_{119Sn-C} C₆H₅-C=*C*H-Sn = 421 Hz, ${}^{2}J_{119Sn-C}$ C₆H₅-C=CH-Sn = 65 Hz, ${}^{1}J_{117Sn-C}$ C₆H₅-C=CH-Sn = 401 Hz, ${}^{2}J_{117Sn-C}$ C₆H₅-C=CH-Sn = 62 Hz), 152.2 $({}^{1}J_{{}^{119}Sn-C} i-C_{6}H_{5}-Sn = 91 Hz, {}^{2}J_{{}^{119}Sn-C} i-C_{6}H_{5}-Sn = 53 Hz, {}^{1}J_{{}^{117}Sn-C}$ $i-C_6H_5-Sn = 94$ Hz, ${}^2J_{117}Sn-C$ $i-C_6H_5-Sn = 53$ Hz), 169.5 (${}^1J_{119}Sn-C$ $C_6H_5-C=CH-Sn = 415$ Hz, ${}^2J_{119Sn-C}$ $C_6H_5-C=CH-Sn = 37$ Hz, ${}^{1}J_{117Sn-C}$ C₆H₅-C=CH-Sn = 379 Hz, ${}^{2}J_{117Sn-C}$ C₆H₅-C=CH-Sn = 37 Hz), 119 Sn{¹H} NMR (C₆D₆) δ (ppm): *E* -54.45, -66.35, Z-49.39, 65.91, -83.59 (unreacted **3b**).‡

COMPOUND 9: REACTION OF 3A WITH 2 EQUIV. OF PHENYLACETYLENE. The experiment to prepare 4b was repeated with a 1:2 ratio of the distannane 3a and phenylacetylene and the reaction mixture analyzed after 72 h.

The distannane **3a** (1.55 g, 4.7 mmol), phenylacetylene (966 mg, 9.4 mmol) and Pd(PPh₃)₄ (10 mg, 8.6 × 10⁻³ mmol) were weighed into a reaction flask in a glove box. The neat reaction mixture was heated (80 °C) for 72 h. Initial ¹¹⁹Sn NMR (C_6D_6) revealed peaks identified as the *cis* and *trans* isomers of compound **4b** along with unreacted **3a**. The sample was heated at 80 °C for an additional 72 h and again analyzed by ¹¹⁹Sn NMR, confirming all of the unreacted **3a** was consumed. The crude brown semi-solid product was left in the NMR tube and crystals were formed after two weeks. Analysis of the crystalline product **9** (¹¹⁹Sn NMR) displays a single resonance at

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-44.01 ppm. The crystal structure of this product reveals two phenylacetylene units inserted between two tin atoms. The crystalline product contained a carbon backbone that was entirely the *cis* isomer, *i.e.*, (*Z*,*Z*)-1,4-bis(trimethylstannyl)-1,4-diphenyl-buta-1,3-diene, **9**. Yield = 1.07 g (43%).

¹H NMR (C₆D₆) δ (ppm): 0.25 (s, 18H, ²J_{119Sn-H} (Sn-CH₃) = 54 Hz, ²J_{117Sn-H} (Sn-CH₃) = 52 Hz), 7.02–7.31 (m, 10H, C₆H₅–), 7.41 (s, 2H, ²J_{119Sn-H} (=CH-Sn) = 21 Hz, ²J_{117Sn-H} (=CH-Sn) = 21 Hz, ¹³C{¹H} NMR (C₆D₆) δ (ppm): –7.28 (C₆H₅–C–Sn–CH₃), 126.32 (*p*-C₆H₅), 126.88 (*m*-C₆H₅), 128.60 (*o*-C₆H₅), 143.48 (C₆H₅–C=CH–), 147.13 (i-C₆H₅), 153.63 (C₆H₅–C=CH–Sn), ¹¹⁹Sn{¹H} NMR (C₆D₆) δ (ppm): –44.01. UV-VIS: λ_{max} (THF)/nm 309 (ε /dm³ mol⁻¹ cm⁻¹ 1400). HRMS (70 eV): *m*/*z* calc. for C₂₂H₃₀Sn₂ 534.2041, not observed, calc. *m*/*z* 519.1841 (M⁺ – CH₃), found *m*/*z* 519.2036.

COMPOUND 12: PREPARATION OF $[(n-Bu)_2 Sn]_n$. The parent polystannane, $[(n-Bu)_2 Sn]_n$, **12** was prepared according to the method described by Caseri *et al.*^{1f} in good yield (>90%). Polymer **12** was recovered from dehydropolymerization of $(n-Bu)_2 SnH_2$ in CH₂Cl₂ using Wilkinson's catalyst. ¹¹⁹Sn{¹H} NMR (C₆D₆) δ (ppm): -190.7. λ_{max} (THF)/nm 380 (ε /dm³ mol⁻¹ cm⁻¹ 760).

COMPOUND 13A: REACTION OF 12 WITH ACETYLENE. Under an inert atmosphere $(N_2(g))$ and protected from ambient light sources, the yellow coloured polymer 12 (1 g, 4.3 mmol) and $Pd(PPh_3)_4$ (40 mg, 3.5×10^{-2} mmol) were dissolved in 20 mL of 1,4dioxane and transferred to a 3-neck flask equipped with septa and two gas inlets. Acetylene gas was passed through the reaction mixture and the contents heated to reflux temperature (85 °C) for 100 h. A small amount of the reaction mixture was sampled from the reaction flask. The ¹¹⁹Sn NMR spectrum revealed new resonances at 68.51, -50.23, -66.60 and -176.83 ppm, and the absence of a resonance at -190 ppm for the parent polymer (12). The solvent was removed under reduced pressure, redissolved in a small amount of CH₂Cl₂ and then triturated with excess dry methanol. The opaque solution was placed in a glove box freezer (-33 °C) overnight and thereafter a yellow solid was recovered. The ¹¹⁹Sn NMR revealed a single peak at -66.5 ppm for the new polymer (13a).¶

¹H NMR (C₆D₆) δ (ppm): 0.8–2.0 (m, 54H, CH₃CH₂CH₂CH₂-Sn, CH₃CH₂CH₂CH₂-Sn, CH₃CH₂CH₂CH₂-Sn), 7.40 (br s, 2H, (-Sn–CH=), ¹³C{¹H} NMR (C₆D₆) δ (ppm): 11.18 (CH₃CH₂CH₂CH₂CH₂-Sn), 14.28 (CH₃CH₂CH₂CH₂-Sn), 29.33 (CH₃CH₂CH₂CH₂CH₂-Sn), 30.82 (CH₃CH₂CH₂CH₂-Sn, 167.60 (-Sn–CH=), ¹¹⁹Sn{¹H} NMR (C₆D₆) δ (ppm): -66.5. UV-VIS: λ_{max} (THF)/nm 320 (ε /dm³ mol⁻¹ cm⁻¹ 80). Found: C, 48.41, H, 6.60. Calc. for C₂₆H₅₆Sn₃: C, 47.64, H, 7.52%.

COMPOUND 13B: REACTION OF 12 WITH PHENYLACETYLENE. First attempt: Under an inert atmosphere $(N_2(g))$ and protected from ambient light sources, the yellow coloured polymer 12 (500 mg, 2.2 mmol), phenylacetylene (150 mg, 1.5 mmol) and

§Values for trans isomer in square brackets. Sn-Sn couplings not resolved.

 $[\]P$ Trace PPh₃ and PPh₃O were evident by NMR (¹H and ¹³C) and could not be effectively removed due to the solubility of polymer **13a** in almost all solvents.

 $Pd(PPh_3)_4$ (10 mg, 8.6×10^{-3} mmol) were dissolved in 20 mL of 1,4-dioxane and transferred to a Schlenk flask. The reaction mixture was heated to reflux temperature (85 °C) for 100 h. The ¹¹⁹Sn NMR spectrum revealed new resonances at 89.0 ppm, along with two small peaks at –190 ppm for the parent polymer (12) and at –201 for cyclic oligomers.

Second attempt: Under an inert atmosphere $(N_2(g))$ and protected from ambient light sources, the yellow coloured polymer **12** (800 mg, 3.4 mmol) phenylacetylene (250 mg, 2.4 mmol) and Pd(PPh₃)₄ (15 mg, 1.3×10^{-2} mmol) were reacted neat in a Schlenk flask. The reaction mixture was heated to 85 °C for 100 h. The ¹¹⁹Sn NMR spectrum revealed resonances at –66.1 ppm and –190.6 ppm.

¹H NMR (C₆D₆) δ (ppm): 0.8–2.0 (m, 54H, CH₃CH₂CH₂CH₂-Sn, CH₃CH₂CH₂-Sn, CH₃CH₂CH₂-Sn), 6.94–7.40 (m, 5H, C₆H₅), 7.52 (m, 1H, (–Sn–CH=), ¹³C{¹H} NMR (C₆D₆) δ (ppm): 11.75 (CH₃CH₂CH₂CH₂-Sn), 14.05 (CH₃CH₂CH₂CH₂-Sn), 28.68 (CH₃CH₂CH₂CH₂-Sn), 33.67 (CH₃CH₂CH₂CH₂-Sn), 28.68 (CH₃CH₂CH₂CH₂-Sn), 33.67 (CH₃CH₂CH₂CH₂-Sn), 126.65 (*p*-C₆H₅), 129.22 (*m*-C₆H₅), 131.70 (*o*-C₆H₅), 132.49 (C₆H₅-C=CH-Sn), 159.40 (–Sn–CH=CPh), 167.60 (–Sn–CH=CPh), ¹¹⁹Sn{¹H} NMR (C₆D₆) δ (ppm): –66.1, –190.6. UV-VIS: λ_{max} (THF)/nm 370 (ε /dm³ mol⁻¹ cm⁻¹ 970). Found: C, 48.98, H, 6.62. Calc. for C₃₂H₆₀Sn₃: C, 49.14, H, 8.01%.

Crystal structure determination

Data for the X-ray structure determination of **9** was collected on a Bruker-Nonius Kappa-CCD diffractometer using monochromated Mo-K α radiation ($\lambda = 0.70926$ Å) and were measured using a combination of ϕ scans and ω scans with κ offsets, to fill the Ewald sphere. The data were processed using the Denzo-SMN package.²⁷ Absorption corrections were carried out using SORTAV.²⁸ The structure was solved and refined using SHELXTL V6.1²⁹ for full-matrix least-squares refinement that was based on F^2 . All H atoms were included in calculated positions and allowed to refine in riding-motion approximation with U_{iso} tied to the carrier atom.

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