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for contraction of the iron and ruthenium complexes are the same, at room temperature the iron complex **20b** undergoes migratory insertion at least 10^7 times faster than its ruthenium analogue.

The net result of a carbene migratory insertion is formation of a carbon–carbon single bond at the expense of a carbon–metal double bond. Inasmuch as rearrangement of **1** and **20b** is endothermic, their transition states should resemble the 16-electron intermediate products and differences in their respective energies should therefore be reflected in differences in the strengths of their carbon–metal double bonds.[20] The generally accepted presumption that second-row transition-metal carbon–metal bonds are stronger than those of first-row metals[21] therefore provides an attractive explanation for this difference in rates.

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Supplementary Material Available: Text giving experimental procedures for the preparation of **20a** and **20b** by the ring-closure method (5 pages). Ordering information is given on any current masthead page.

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(20) Carter, E. A.; Goddard, W. A., III. *Organometallics* **1988**, *7*, 675.

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A New Strategy for the Synthesis of Homologously Pure Linear Polystannane Oligomers[†]

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Summary: The reagent **6** is utilized for the stepwise synthesis of linear polystannane oligomers in which hydrostannolysis is employed as the Sn–Sn bond-forming reaction, and DIBAL-H is used to regenerate a new Sn–H functionality for extended chain growth through repetition of the two-step reaction sequence. The electronic spectra of these oligomers are influenced by chain length and the specific placement of substituents, as demonstrated by the homologous series **7**, **9**, and **13–15** and the phenylated di- and tristannanes **18–20**.

New types of protecting groups should greatly aid molecular engineering approaches to inorganic or organometallic materials that require the construction of complex structures via rational routes.[1] Herein, we describe application of the β-alkoxy substituent as a protecting group for the programmable stepwise synthesis of linear polystannane oligomers $R-(R_2Sn)_n-R$ (**1**), a class of compounds that exhibit interesting optical properties[2] and which, to date, have not been routinely available for study.[3]

Our approach to polystannane oligomers is based on the tin–tin bond-forming hydrostannolysis reaction,[4] which has been successfully used for the high-yielding syntheses of linear tri- and tetrastannanes according to reaction 1.[5]

$$\mathrm{H\text{-}(R_2Sn)_n\text{-}H} \quad + \quad 2\ \mathrm{R_3SnNMe_2} \xrightarrow[n\,=\,1 \text{ or } 2]{} \mathrm{R_3Sn\text{-}(R_2Sn)_n\text{-}SnR_3} \quad + \quad 2\ \mathrm{HNMe_2} \tag{1}$$

However, in order to apply this synthetic methodology to the construction of higher order homologues, a protecting group is required that can be removed, after hydrostannolysis, to reveal a new functionality that can then serve as the site for extended chain growth of the polystannane backbone. As Schemes I and II show, this requirement is met by the β-alkoxy substituent.

An equimolar mixture of the diorganotin dihydride **2** and the diorganotin dichloride **3** generates, in situ, the diorganotin hydridochloride species **4**, and this species is more reactive toward hydrostannation than **2** (Scheme I).[6] Thus, addition of a radical initiator and ethyl vinyl ether to a solution of **4** in hexane regiospecifically produces compound **5**,[7] which is subsequently converted, without

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[†] Contribution No. 8431.

(1) Gomez, F. A.; Johnson, S. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1991**, *113*, 5915.

(2) (a) Drenth, W.; Janssen, M. J.; Van Der Kerk, G. J. M.; Vliegenthart, J. A. *J. Organomet. Chem.* **1964**, *2*, 265. (b) Drenth, W.; Noltes, J. G.; Bulten, E. J.; Creemers, H. M. J. C. *J. Organomet. Chem.* **1969**, *17*, 173. (c) Adams, S.; Dräger, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1255.

(3) (a) Neumann, W. P.; Konig, K. *Justus Liebigs Ann. Chem.* **1964**, *677*, 1. (b) Creemers, H. M. J. C.; Noltes, J. G. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 382. (c) Jousseaume, B.; Chanson, E.; Bevilacqua, M.; Saux, A.; Pereyre, M.; Barbe, B.; Petraud, M. *J. Organomet. Chem.* **1985**, *294*, C41. (d) Reference 2c.

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(5) Sommer, R.; Schneider, B.; Neumann, W. P. *Justus Liebigs Ann. Chem.* **1966**, *692*, 12.

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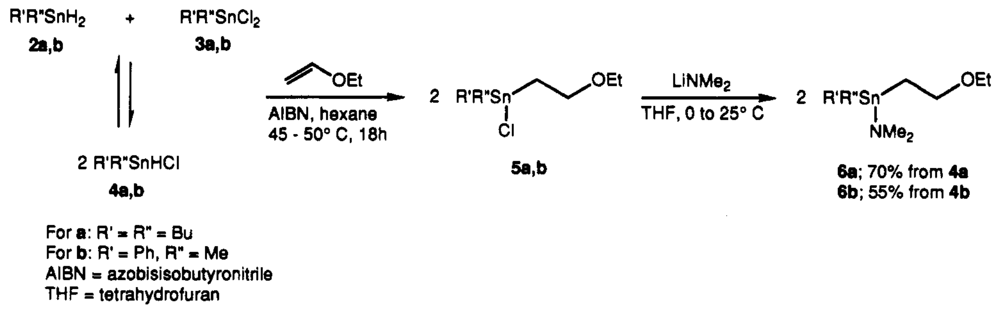
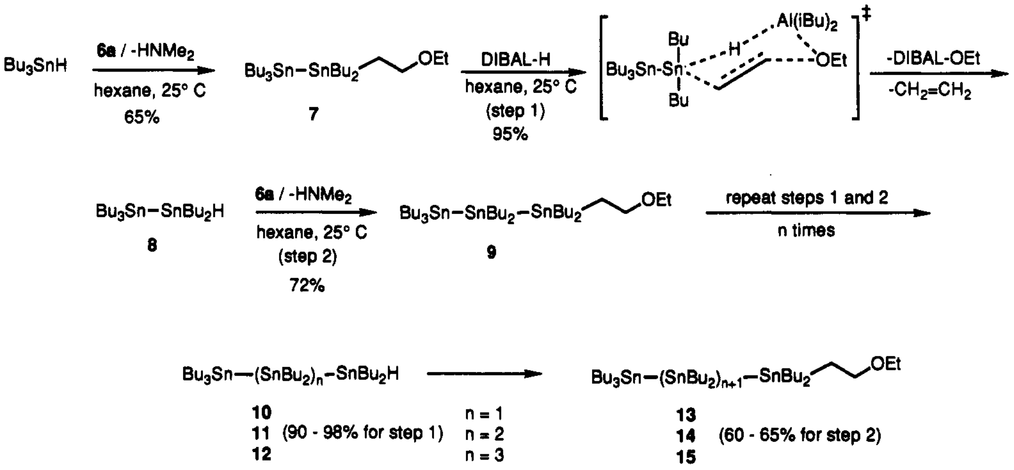
(7) To a solution of 10.34 g (34 mmol) of dichlorodibutylstannane in 80 mL of hexane was first added 8.00 g (34 mmol) of dibutylstannane, followed by 20 mL (210 mmol) of ethyl vinyl ether and 100 mg (0.61 mmol) of azobis(isobutyronitrile). The mixture was then placed into a 150-mL heavy-walled glass Schlenk tube, which was sealed and heated at 45 °C for 18 h. After it was cooled, the reaction vessel was opened in a glovebox, the solvents were removed in vacuo, and the residue was filtered through a $^1/_4$-in. pad of Celite in a glass pipet equipped with a plug of Kimwipe to provide 22.16 g (65 mmol; 96% yield) of the desired product as a clear colorless oil. The purity of this material, as determined by ^{1}H NMR spectroscopy, is adequate for the preparation of **6a**. Note: attempts to further purify **5a** by distillation under reduced pressure result in substantial decomposition. ^{1}H NMR (500 MHz, benzene-d_6): δ 0.83 (t, 3 H, J = 6.9 Hz), 0.89 (t, 6 H, J = 7.0 Hz), 1.23 (m, 4 H), 1.35 (sext, 4 H, J = 7.7 Hz), 1.65 (t, 2 H, J = 7.6 Hz), 1.69 (m, 4 H), 2.97 (q, 2 H, J = 7.0 Hz), 3.28 (t, 2 H, J = 7.5 Hz [$^3J(^{119}\mathrm{Sn}-^1\mathrm{H})$ = 68.5 Hz]).

Scheme I



Scheme II[a]



[a] DIBAL = diisobutylaluminum.

purification, to 6[8] with lithium dimethylamide.[9]

Utilization of 6 for the construction of linear polystannanes was documented by the series of reactions shown in Scheme II.[9] Accordingly, addition of tributylstannane to a solution of 6a in hexane resulted in formation of the distannane 7.[10] This compound was then treated with 1 equiv of diisobutylaluminum hydride (DIBAL-H) in hexane, at room temperature, to generate a Sn–H functional

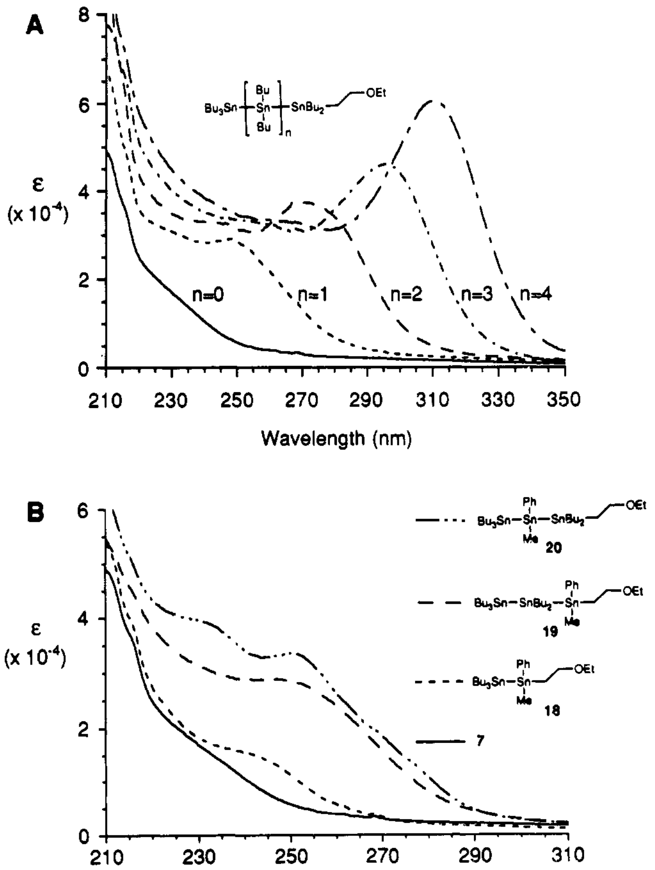


Figure 1. Comparisons of the electronic spectra (in hexane) for (A) the homologous series of 7, 9, and 13–15 and (B) the di- and tristannanes 7 and 18–20.

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[8] To a solution of 22.16 g (65 mmol) of 5a in 100 mL of tetrahydrofuran (THF), cooled to 0 °C, was added dropwise a solution of 3.64 g (71 mmol) of lithium dimethylamide in 60 mL of THF. After the addition was complete, the reaction mixture was warmed to room temperature and stirred for 1 h. In a glovebox, the solvent was removed in vacuo, the residue taken up in hexane, and the solid material removed by filtration through a 1 × 2 cm pad of Celite. Upon removal of the solvent from the filtrate, 21.35 g of the crude product was obtained as a dark yellow oil. This material was then distilled at 85 °C (0.25 mmHg) to provide 16.65 g (47.6 mmol; 73% yield) of 6a as an extremely moisture-sensitive colorless liquid. ^{1}H NMR (500 MHz, benzene-d_6): δ 0.93 (t, 6 H, J = 7.0 Hz), 1.02 (m, 4 H), 1.07 (t, 3 H, J = 7.0 Hz), 1.32 (t, 2 H, J = 7.6 Hz), 1.37 (sext, 4 H, J = 7.4 Hz), 1.61 (m, 4 H), 2.83 (s, 6 H [$^3J(^{119/117}\mathrm{Sn}-^1\mathrm{H})$ = 36.6 Hz]), 3.22 (q, 2 H, J = 6.9 Hz), 3.51 (t, 2 H, J = 7.6 Hz [$^3J(^{119}\mathrm{Sn}-^1\mathrm{H})$ = 63.0 Hz]). Anal. Calcd for $C_{14}H_{33}NOSn$: C, 48.03; H, 9.50; N, 4.00. Found: C, 47.69; H, 9.62; N, 4.36.

[9] Detailed information on the preparation and characterization of all new compounds is provided in the supplementary material.

[10] To a solution of 6 g (17.1 mmol) of 6a in 15 mL of hexane was slowly added dropwise a solution of 5 g (17.1 mmol) of tributylstannane in 15 mL of hexane, at room temperature. After the addition was complete, the mixture was stirred for 3 h and then the solvent was removed in vacuo to give a slightly yellow oil. This was taken up in a minimum volume of hexane and the solution applied to a silica gel chromatography column (ca. 8 cm × 10 cm) preequilibrated with hexane. Elution with hexane as the solvent was continued until TLC showed that the material traveling at the solvent front was removed. At this point, the eluant was changed to a 20:1 hexane/diethyl ether solvent mixture and elution continued until the product had eluted. Removal of the solvent from the combined fractions provided 6.5 g (10.9 mmol) (65% yield) of 7. ^{1}H NMR (500 MHz, benzene-d_6): δ 1.00–1.82 (multiplets, 50 H), 3.35 (q, 2 H, J = 6.9 Hz), 3.68 (t, 2 H, J = 7.2 Hz). UV (hexane): λ_{max} <215 nm. Anal. Calcd for $C_{24}H_{54}OSn_2$: C, 48.36; H, 9.13. Found: C, 48.09; H, 8.89.

group and quantitatively produce, as determined by ^{1}H NMR spectroscopy, the distannane **8** (95% isolated yield).[11] As the reaction proceeds, rapid gas evolution, presumably ethylene, is observed and the only other product obtained is diisobutylaluminum ethoxide (DIBAL-OEt). At the present time, we believe that this transformation occurs through the intermediacy of the six-center transition-state complex shown in Scheme II. Treatment of **8** with **6a** provides the tristannane **9**, and then the two-step homologation process is repeated several times to produce the two series of air-sensitive, homologously pure polystannane oligomers represented by compounds **10**–**12** and **13**–**15**.[12] With regard to this methodology, it is interesting to note that the two-step process for chain homologation can be carried out as a "one pot" procedure, since the presence of the DIBAL-OEt which is initially formed does not interfere with the subsequent hydrostannolysis reaction.

Concerning the electronic spectra of polystannanes, those displayed in Figure 1A for the homologous series **7**, **9**, and **13**–**15** show a red-shifting of the lowest energy transition with increasing chain length similar to that previously reported for the series $Et{-}(Et_2Sn)_n{-}Et$ (n = 2–6; **16**)[2b] and for $Ph_3Sn{-}(t\text{-}Bu_2Sn)_n{-}SnPh_3$ (n = 1–4; **17**).[2c] However, the specific positions and magnitudes of these transitions are quite different for the three series. For example, where n = 5 and 6 in **16**, λ_{max} is 310 nm (ϵ_{max} 21 380) and 325 nm (ϵ_{max} 27 542), respectively.[13] In contrast, the corresponding values for **14** and **15** are λ_{max} 296 nm (ϵ_{max} 46 040) and λ_{max} 310 nm (ϵ_{max} 60 687), respectively. In this case, it is likely that the differences between these two series can be attributed to the determination by Jousseaume et al.[3c] that inhomogeneous material is obtained by the synthetic methodology previously used to prepare the oligomers of **16**. For **17**, however, the red-shifting of the lowest energy transitions in this series relative to those in Figure 1A and the observed decrease in their intensities with increasing chain length are differences that are undoubtedly a function of the strong nonbonded steric interactions among the organic substituents in **17** which severely restrict conformational mobility[14] and produce an increase in the mean Sn–Sn bond length of the polystannane backbone with increasing chain length.[2c] Clearly, further studies are still required to elucidate more precisely the structure/property relationships that govern the optical properties of polystannanes, and in this regard, as the different electronic spectra of **7** and the phenylated di- and tristannanes **18**–**20** demonstrate (Figure 1B), the synthetic methodology of Schemes I and II should allow one to systematically probe the impact that different types of substituents (i.e. alkyl vs aryl) and different patterns of substitutions have on the electronic structure of these materials.

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Supplementary Material Available: Additional experimental details and spectroscopic data for new compounds (4 pages). Ordering information is given on any current masthead page.

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[11] To a solution of 2.18 g (3.7 mmol) of **7** in 15 mL of hexane was slowly added dropwise a solution of 0.57 g (4.0 mmol) of DIBAL-H in 10 mL of hexane, at room temperature. After the addition was complete, the mixture was stirred for 1 h, at which time TLC (20:1 hexane/Et_2O) showed no trace of the starting material (R_f 0.44). The solvent was removed in vacuo, the residue taken up in the minimum amount of hexane, and the solution applied to a silica gel column (ca. 4 cm × 5 cm) preequilibrated with hexane. At this point, gas evolution, presumably isobutane, occurs due to hydrolysis of DIBAL-OEt. Elution with hexane and collection of the material traveling at the solvent front provided 1.88 g (3.6 mmol; 95%) of **8** as a colorless oil after removal of the solvent. ^{1}H NMR (500 MHz, benzene-d_6): δ 1.00–1.82 (multiplets, 45 H), 4.76 (quint, 1 H, $^3J(CH_2{-}SnH)$ = 2 Hz, $^1J(^{119}Sn{-}^1H)$ = 1390 Hz, $^2J(^{119/117}Sn{-}^1H)$ = 105 Hz). IR: ν(Sn–H) 1792 cm^{-1}. UV: $\lambda_{max} < 215$ nm. Anal. Calcd for $C_{20}H_{46}Sn_2$: C, 45.85; H, 8.85. Found: C, 45.65; H, 8.74.

[12] Representative procedures are as follows: (a) To a solution of 250 mg (0.19 mmol) of **14** in 1 mL of hexane was added dropwise a solution of 35 mg (0.25 mmol) of DIBAL-H in 0.5 mL of hexane, at room temperature. The reaction was worked up in the usual manner as described above for **8** (column size 2 cm × 3 cm); yield of **12** 230 mg (0.18 mmol; 98%). ^{1}H NMR (500 MHz, benzene-d_6): δ 1.00–1.82 (multiplets, 99 H), 5.00 (quint, 1 H, $^3J(CH_2{-}SnH)$ = 2 Hz, $^1J(^{119}Sn{-}^1H)$ = 1387 Hz, $^2J(^{119/117}Sn{-}^1H)$ = 105 Hz, $^3J(^{119/117}Sn{-}^1H)$ = 22 Hz). IR: ν(Sn–H) 1784 cm^{-1}. UV: λ_{max} 293 nm (ϵ_{max} 30 840). Anal. Calcd for $C_{44}H_{100}Sn_5$: C, 43.22; H, 8.24. Found: C, 43.39; H, 8.16. (b) To a solution of 62 mg (0.18 mmol) of **6a** in 2 mL of hexane was added dropwise a solution of 200 mg (0.16 mL) of **12** in 1 mL of hexane. After it was stirred for 3 h, the reaction mixture was worked up in the usual manner as described above for **7** (column size 2 cm × 3 cm); yield of **15** 150 mg (0.10 mmol; 62%). ^{1}H NMR (500 MHz, benzene-d_6): δ 1.00–1.82 (multiplets, 122 H), 3.41 (q, 2 H, J = 7.0 Hz), 3.76 (t, 2 H, J = 7.7 Hz). UV: λ_{max} 310 (ϵ_{max} 60 687). Anal. Calcd for $C_{56}H_{126}OSn_6$: C, 44.02; H, 8.31. Found: C, 44.18; H, 8.18.

[13] Creemers, H. M. J. C.; Noltes, J. G. *J. Organomet. Chem.* **1967**, *7*, 237.

[14] Experimental and theoretical investigations of disordered polysilanes, $R{-}(R_2Si)_n{-}R$, conclude that their electronic spectra arise from the additive contributions of a variety of chromophoric segments differing in length and absorption peak wavelength, a chromophore segment in this case being visualized as an approximately planar, all-trans chain segment terminated by stronger twists (e.g. gauche). For a recent review, see: Balaji, V.; Michl, J. *Polyhedron* **1991**, *10*, 1265.