Lewis Acid-Catalyzed Hydrostannation of Acetylenes. Regio- and Stereoselective *Trans*-Addition of Tributyltin Hydride and Dibutyltin Dihydride[†]

Naoki Asao,[‡] Jian-Xiu Liu, Tomoko Sudoh, and Yoshinori Yamamoto*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-77, Japan

Received December 28, 1995[⊗]

Lewis acids such as $ZrCl_4$ or $HfCl_4$ catalyze the hydrostannation of acetylenes **1** by tributyltin hydride to produce the *cis* vinylstannanes **2** by regio- and stereoselective *anti*-hydrostannation. The hydrostannation of acetylenes using dibutyltin dihydride was also catalyzed by $ZrCl_4$ to give the stereodefined *Z-Z* divinyltin derivatives **4** by an *anti*-hydrostannation pathway. The use of nonpolar solvents such as toluene or hexane was essential for obtaining high stereoselectivity and chemical yield. Since $ZrCl_4$ and $HfCl_4$ are not soluble in such solvents, the hydrostannations were carried out in a heterogeneous system. The reactions of internal acetylenes with Bu_3SnH proceeded smoothly, although the use of stoichiometric amounts of $ZrCl_4$ gave better results. The $ZrCl_4$-catalyzed hydrostannation at 0 °C gave better yields and stereoselectivities than the reaction at room temperature. To help clalify the reason, the reaction of Bu_3SnH with $ZrCl_4$ was monitored by ^1H and ^{119}Sn NMR spectroscopy, and it was found that Bu_3SnH reacted with $ZrCl_4$ at room temperature to afford a mixture of tributyltin hydride, dibutyltin dihydride, and tetrabutyltin.

Hydrostannation[1] of acetylenes is one of the simplest and the most straightforward preparation methods for vinylstannanes, which have great versatility as building blocks in synthesis.[1a,2] It is well known that the hydrostannation of acetylenes by R_3SnH is induced by either (1) radical initiators[3] or (2) transition metal catalysts.[4] The radical-induced procedure often provides a mixture of *trans*- and *cis*-hydrostannation products, since isomerization of the alkenyltin products occurs in the presence of tin radicals.[5,6] Although the transition metal-catalyzed reaction proceeds with high stereoselectivity via a *syn*-hydrostannation pathway, it usually produces a mixture of two regioisomers: one by addition of the Bu_3Sn group to the terminal acetylenic carbon (terminal addition product) and the other by addition of the Bu_3Sn group to the internal acetylenic carbon (internal addition product). As for hydrostannations using R_2SnH_2, little attention has been directed toward the stereocontrolled formation of divinyltin derivatives.[7] Recently we reported that the hydrostannation process was catalyzed dramatically by a Lewis acid such as $ZrCl_4$ or $HfCl_4$, and that the $ZrCl_4$ catalyzed procedure produced the *cis* vinylstannanes by regio- and stereoselective *anti*-hydrostannation.[8] In this paper, we detail this new hydrostannation method and report that hydrostannations with dibutyltin dihydride to form regio- and stereodefined hydrostannated divinyltin derivatives are also catalyzed by $ZrCl_4$.

Results and Discussion

The results of hydrostannation using tributyltin hydride are summarized in Table 1. The reaction of 1-octyne **1a** with Bu_3SnH in the presence of 1.1 equiv of $ZrCl_4$ in toluene gave the *anti*-hydrostannation product **2a** (*Z*-vinylstannane) regio- and stereoselectively in 30% yield (entry 1).[9] Although the yield of **2a** was low, the stereoisomer **3a** (*E*-vinylstannane) was not detected in the ^1H NMR spectrum of the reaction product. The chemical yield was enhanced to 76% by using 0.2 equiv of $ZrCl_4$ (entry 2), and the use of hexane as a solvent resulted in an 89% yield (entry 3). It should be noted that $ZrCl_4$ is not soluble in toluene and hexane at 0 °C, and therefore the reaction is carried out in a heterogeneous system. The use of THF and CH_2Cl_2, solvents that dissolve the catalyst more effectively than the non-polar solvents, gave lower stereoselectivity and chemical yield. $HfCl_4$ was also an efficient catalyst for the hydrostannation (entry 4), but the reaction was slightly slower than that with $ZrCl_4$. The use of a typical Lewis acid of group 14, $AlCl_3$, as a catalyst afforded a 60:40 mixture of **2a** and **3a** in 53% yield.

We examined the $ZrCl_4$-catalyzed hydrostannation of several other alkynes. The reaction of phenylacetylene

---

[†] Dedicated to Clayton H. Heathcock on the occasion of his 60th birthday.

[‡] Present address: Department of Chemistry, Graduate School of Science, Hokkaido University.

[⊗] Abstract published in *Advance ACS Abstracts*, June 1, 1996.

(1) (a) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987. (b) Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1967**, *9*, 295. (c) Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1967**, *9*, 285.

(2) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

(3) (a) The use of AIBN as a radical initiator; ref 1. (b) The use of Et_3B: Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547. Nozaki, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3465. (c) The use of ultrasound; Nakamura, E.; Imanishi, Y.; Machii, D. *J. Org. Chem.* **1994**, *59*, 8178. Nakamura, E.; Machii, D.; Inubushi, T. *J. Am. Chem. Soc.* **1989**, *111*, 6849.

(4) (a) Pd catalysts; Ichinose, Y.; Oda, H.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3468. Zhang, H. X.; Guibe, F.; Balavoine, G. *Tetrahedron Lett.* **1988**, *29*, 619. Miyake, H.; Yamamura, K. *Chem.Lett.* **1989**, 981. (b) Rh catalysts; Kikukawa, K.; Umekawa, F.; Wada, G.; Matsuda, T. *Chem. Lett.* **1988**, 881. (c) Mo catalysts; Zhang, H. X.; Guibe, F.; Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1857.

(5) (a) Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1968**, *11*, 541. (b) Nativi, C.; Taddei, M. *J. Org. Chem.* **1988**, *53*, 820.

(6) The sonochemical hydrostannation produces the *anti*-hydrostannation product stereoselectively (ref 2c).

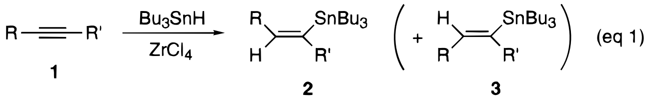
(7) The cyclic divinyltin derivatives were produced by the hydrostannation of diynes under heat conditions. Keusink, A. J.; Nottes, J. G.; Bussing, H. A.; van der Kerk, G. J. M. *Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 1036. Ashe, A. J., III; Shu, P. *J. Am. Chem. Soc.* **1971**, *93*, 1804 and references cited therein.

(8) Asao, N.; Liu, J.-X.; Sudoh, T.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.*, **1995**, 2405.

(9) As a byproduct, 1-octene was produced.

S0022-3263(95)02273-0 CCC: $12.00

Table 1. Lewis Acid-Catalyzed Hydrostannation of Acetylenes with Bu_3SnH[a]

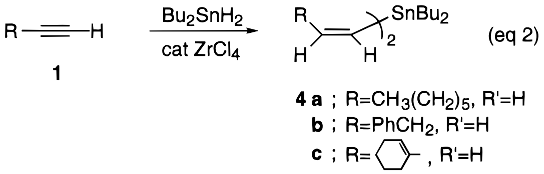


a ; R=$CH_3(CH_2)_5$, R'=H
b ; R=Ph, R'=H
c ; R=*p*-Me-C_6H_4, R'=H
d ; R=TBDMSO$(CH_2)_3$, R'=H
e ; R=BnO$(CH_2)_3$, R'=H
f ; R=$CH_3(CH_2)_5$, R'=Cl
g ; R=R'=$CH_3(CH_2)_4$
h ; R=R'=Ph

		1				
entry	Lewis acid (equiv)	R	R′		yield, %[b]	*Z*-:*E*-isomer **2**:**3**
1	$ZrCl_4$ (1.1)	$CH_3(CH_2)_5$	H	(**1a**)	30	>95:5
2	$ZrCl_4$ (0.2)	$CH_3(CH_2)_5$	H	(**1a**)	76	>95:5
3[d]	$ZrCl_4$ (0.2)	$CH_3(CH_2)_5$	H	(**1a**)	89	>95:5
4	$HfCl_4$ (0.2)	$CH_3(CH_2)_5$	H	(**1a**)	86	>95:5
5	$ZrCl_4$ (0.2)	Ph	H	(**1b**)	73 (40)	95:~5
6	$ZrCl_4$ (0.2)	*p*-Me-C_6H_4	H	(**1c**)	84	>95:5
7	$ZrCl_4$ (0.2)	TBDMSO$(CH_2)_3$	H	(**1d**)	87 (48)	>95:5
8	$ZrCl_4$ (0.2)	BnO$(CH_2)_3$	H	(**1e**)	0[e]	–
9	$ZrCl_4$ (0.2)	$CH_3(CH_2)_5$	Cl	(**1f**)	47 (40)	>95:5
10	$ZrCl_4$ (1.0)	$CH_3(CH_2)_4$	$CH_3(CH_2)_4$	(**1g**)	56	>95:5
11	$ZrCl_4$ (1.0)	Ph	Ph	(**1h**)	33[f]	>95:5

[a] Reactions were conducted in toluene at 0 °C under Ar less otherwise noted. [b] Determined by ^1H NMR spectra of the reaction product using *p*-xylene as an internal standard. Isolated yields were indicated in the parentheses. The C–Sn bond of the product was cleaved readily at the purification stage using silica-gel column chromatography. [c] Determined by 270 MHz ^1H NMR spectra. The stereoisomers **3** were not detected by the NMR. The ratio, >95:5, came from the limit of detection for the stereoisomer. [d] Hexane was used as a solvent. [e] The starting material (**1e**) was recovered quantitatively. [f] *trans*-Stilbene was obtained in 46% yield in addition to 33% yield of **2h**.

Table 2. Lewis Acid-Catalyzed Hydrostannation of Acetylenes with Bu_2SnH_2[a]



entry	R	1	yield, %[b]	4:other isomers[c]
1	$CH_3(CH_2)_5$	**1a**	85 (60) (**4a**)	>95:5
2	$PhCH_2$	**1j**	78 (54) (**4b**)	>95:5
3	C_6H_9	**1k**	76 (**4c**)	>95:5

[a] Reactions were conducted using 4.0 equiv of **1**, 1.0 equiv of Bu_2SnH_2, and 0.2 equiv of $ZrCl_4$ in toluene at 0 °C under Ar. [b] Determined by ^1H NMR spectra of the reaction product using *p*-xylene as an internal standard. Isolated yields were indicated in the parentheses. Purification of the product using silica-gel column chromatography caused partial protonolysis of the C–Sn bond, leading to significantly low isolated yields. [c] Determined by 270 MHz 1H NMR spectra. The stereoisomers were not detected by the NMR. The ratio, >95:5, came from the limit of detection for the stereoisomer.

(**1b**) gave **2b** in 73% yield along with trace amounts of **3b** (less than 5%) (entry 5), whereas the addition to *p*-tolylacetylene (**1c**) afforded stereoselectively **2c** in 84% yield. The stereoisomer **3c** was not detected (entry 6). The reaction of 5-(*tert*-butyldimethylsilyloxy)-1-pentyne (**1d**) gave **2d** stereoselectively in high yield (entry 7). On the other hand, the addition to 5-(benzyloxy)-1-pentyne (**1e**) did not take place, and the starting material was recovered quantitatively (entry 8). A Lewis acid can coordinate more easily to a BnO group than to the sterically demanding (*t*-Bu)Me_2SiO. It seems that $ZrCl_4$ coordinates to the BnO group of **1e**, instead of acting as a catalyst for the hydrostannation. The $ZrCl_4$-catalyzed hydrostannation of 1-chloro-1-octyne (**1f**) gave **2f** stereoselectively and regioselectively in moderate yield (entry 9). The reactions of 6-dodecyne (**1g**) and tolan (**1h**) also proceeded smoothly, although the use of stoichiometric amounts of $ZrCl_4$ gave better results. Since the vinylstannanes are sensitive to silica gel, purification of **2** by column chromatography on silica gel made the isolated yields down.

The Lewis acid-catalyzed hydrostannation with dibutyltin dihydride also proceeded smoothly to give regio- and stereodefined divinyltin derivatives in good to high yields. The results are summarized in Table 2. To avoid the formation of vinyltin hydride derivatives by the reaction of 1 equiv of acetylenes with 1 equivalent of Bu_2SnH_2, excess amounts of acetylenes were used. Chemical yields were based on Bu_2SnH_2. The reaction of 1-octyne **1a** gave the bis *anti*-hydrostannation product **4a** (*Z-Z* divinylstannane) regio- and stereoselectively in 85% yield (entry 1). In contrast, the reaction of **1a** with Bu_2SnH_2 in the absence of $ZrCl_4$ afforded a mixture of several products, which presumably included three stereoisomers (*Z-Z*, *Z-E*, and *E-E* divinylstannanes). The reactions of 3-phenyl-1-propyne (**1j**) proceeded well with high stereoselectivity (entry 2). The $ZrCl_4$ catalyzed hydrostannation of 1-ethynylcyclohexene (**1k**), a conjugated enyne, gave the *bis*-(1,3-dienyl)tin derivative **4c** in good yield with high regio- and stereoselectivity (entry 3).

It is necessary that the reaction temperature be kept at 0 °C, since both the yield and stereoselectivity decreased if the reaction was carried out at room temperature. To help clarify the reason, we monitored the reaction of Bu_3SnH and $ZrCl_4$ without acetylenes by ^1H and ^{119}Sn NMR spectroscopy, in toluene-d_8 initially at −78 °C under Ar. A signal ascribed to Bu_3SnH was observed at 4.95 ppm at −10 °C (Figure 1a). The mixture was allowed to warm to room temperature, kept at this temperature for a few minutes, and then cooled to −10 °C. At this stage, the sharp peak at 4.95 ppm changed to a broad signal (Figure 1b). At −50 °C, two broad peaks appeared (Figure 1c), which changed to two sharp signals (x and y) at −78 °C (Figure 1d); the signal x, at 4.98 ppm, is ascribed to Bu_3SnH, and the signal y is ascribed to Bu_2SnH_2. These results clearly indicate that the redistribution reaction of Bu_3SnH occurs in the presence of

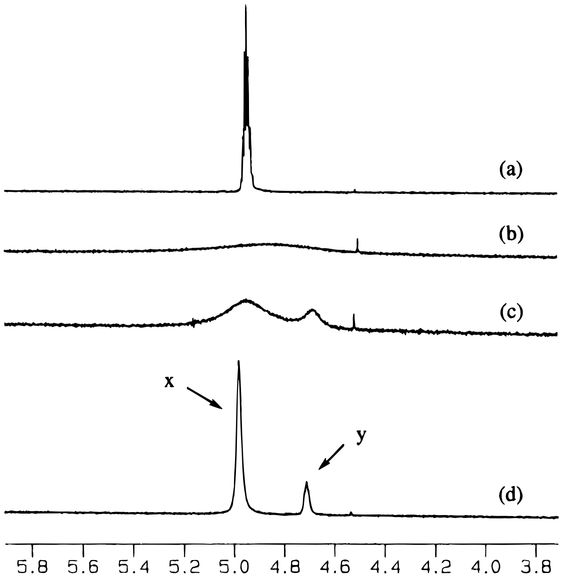
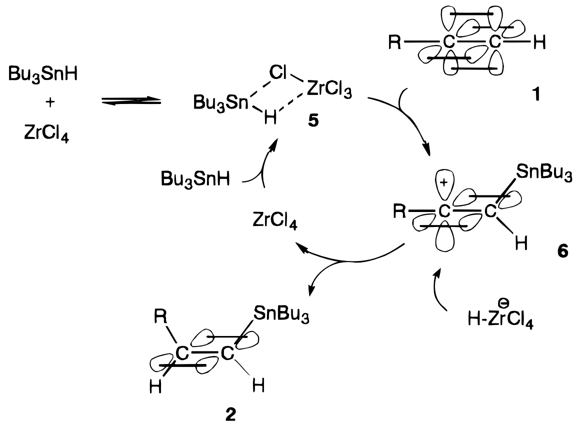


Figure 1. ^{1}H NMR spectra (270 MHz) of a 2:1 mixture of Bu_3SnH and $ZrCl_4$ in toluene-d_8: (a) at −10 °C; (b) at −10 °C (after warming to 0 °C); (c) at −50 °C; (d) at −78 °C. The signal x corresponding to Bu_3SnH and y to Bu_2SnH_2.

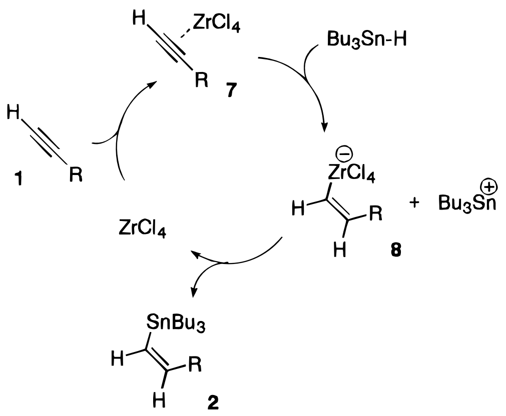
Scheme 1



$ZrCl_4$ to produce Bu_2SnH_2. We also studied the reaction between Bu_3SnH and $ZrCl_4$ by using ^{119}Sn NMR spectroscopy as described above. Three ^{119}Sn signals ascribed to Bu_3SnH, Bu_2SnH_2, and Bu_4Sn were observed at −78 °C. These results demonstrated that Bu_3SnH reacts with $ZrCl_4$ at room temperature to form a complex which leads to a rapid equilibrium between Bu_3SnH, Bu_2SnH_2, and Bu_4Sn. Accordingly, the $ZrCl_4$-catalyzed hydrostannation at room temperature leads to decrease chemical yields of the desired products and the reaction should be carried out at lower temperatures.

Two speculative but plausible mechanisms for the $ZrCl_4$-catalyzed *anti*-hydrostannation are shown in Scheme 1 and 2. The first assumes a rapid equilibrium between $Bu_3SnH + ZrCl_4$ and the reactive species **5** (Scheme 1). It is most probable that the hydrostannation of **1** with **5** proceeds through **6** to give **2** and $ZrCl_4$.[10] Another possibility is that $ZrCl_4$ coordinates to the acetylenic bond faster than to Bu_3SnH to produce complex **7**. A hydride from Bu_3SnH would attack an electron deficient triple bond from the opposite side to $ZrCl_4$ to produce a pentacoordinate zirconium species **8** stereoselectively. This would capture a tributyltin cation with retention of geometry to give **2** and $ZrCl_4$. Similar mechanisms are speculated for the reaction involving Bu_2SnH_2. Although further investigation is needed to establish the mechanism of this $ZrCl_4$-catalyzed reaction, the procedure is synthetically important since the *Z*-alkenyltributylstannanes **2** and **4** are not readily available.

Scheme 2



Experimental Section

General Information. Chemical yields of alkenyltin products were determined from ^{1}H NMR spectra using *p*-xylene as the internal standard. ^{119}Sn NMR spectra (toluene-d_8) were recorded at 100 MHz. Chromatographic separations of tin compounds were performed by using 70−230 mesh silica gel. Precoated silica gel plates Merck F-254 were used for thin-layer analytical chromatography. All solvents were dried before use. Toluene, hexane, and dichloromethane were dried by distillation from phosphorus pentoxide. THF was dried by distillation from sodium and benzophenone. Tributyltin hydride and dibutyltin dihydride were prepared by the reduction of Bu_3SnCl and Bu_2SnCl_2 with $LiAlH_4$, respectively.[11] The following alkynes were commercially available and distilled whenever necessary: 1-octyne, phenylacetylene, *p*-tolylacetylene, 6-dodecyne, diphenylacetylene, 3-phenyl-1-propyne, and 1-ethynyl-1-cyclohexene. *tert*-Butyldimethylsilyl derivative (purified by column chromatography on silica gel, hexane/EtOAc, 20/1) and benzyl derivative (purified by column chromatography on silica gel, hexane/EtOAc, 20/1) of 4-pentyn-1-ol were prepared according to standard procedure.[12] 1-Chloro-1-octyne was prepared according to literature procedure.[13] The following (*E*)-vinyltins were prepared according to literature procedure:[3c] **3c, 3d, 3g,** and **3h**.

Physical and Spectroscopic Characterization of Alkenylstannanes. ^{1}H NMR signals for tributylstannyl groups are found at 1.6−1.2 ppm (m, 12 H) and at 0.9 ppm (m, 15H) in all alkenylstannanes. These values are not included in the listing of ^{1}H NMR resonances. As a rule, MS spectra of alkenyltributylstannanes are characterized by the presence of an important peak (often the base peak) at $M^+ - 57$, which corresponds to the loss of a *n*-butyl fragment. The M^+ peak is, in almost every case, not detected.

Monitoring the Hydrostannation Reaction by ^{1}H and ^{119}Sn NMR spectra (see supplorting information)**.** To a toluene-d_8 solution of Bu_3SnH (1.0 equiv) in a NMR tube was added $ZrCl_4$ (0.5 equiv) at −78 °C under Ar, and this mixture was allowed to warm to −10 °C (NMR no. 1 for ^{1}H and NMR no. 5 for ^{119}Sn; no. 5 includes Bu_4Sn at 0 ppm as an external standard). The mixture was allowed to warm to room tem-

---

[10] In $AlCl_3$-catalyzed hydrosilylation reaction of olefins, a similar silyl hydride−$AlCl_3$ complex was suggested. Yamamoto, K.; Takemae, M. *Synlett* **1990**, 259.

[11] Kerk, G. J. M.; Noltes, J. G.; Luijiten, J. G. A. *J. Appl. Chem.* **1957**, *7*, 366.

[12] Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*; John Wiley: New York, 1991.

[13] Murray, R. E. *Synth. Commun.* **1980**, *10*, 345.

perature, kept at this temperature for a few minutes, and then cooled to −10 °C (NMR no. 2 for ^{1}H and NMR no. 6 for ^{119}Sn; no. 6 includes an external standard). This mixture was cooled to −50 °C (NMR no. 3 for ^{1}H), −55 °C (NMR no. 7 and no. 8 for ^{119}Sn; no. 7 includes an external standard. No. 8 does not include an external standard. The sample of no. 8 was prepared by removal of an external standard from the NMR tube of the sample of no. 7), and −78 °C (NMR no. 4 for ^{1}H).

General Experimental Procedure. Preparation of **2d** from **1d** is representative. To a suspension of $ZrCl_4$ (47 mg, 0.2 mmol) in toluene (0.5 mL) was added **1d** (0.24 mL, 1.0 mmol) at 0 °C under an Ar atmosphere. The mixture was stirred for 5 min, and then Bu_3SnH (0.42 mL, 1.5 mmol) was added. The mixture was stirred for 1 h at 0 °C, and Et_3N (0.07 mL, 0.5 mmol) was added. The mixture was allowed to warm to room temperature, and stirring was continued for 5 min. Hexane was added, and the mixture was filtered through Celite to remove solid material. Removal of the solvents under reduced pressures gave an oily material. The ^{1}H NMR spectra indicated that **2d** was produced in 87% yield.

5-(Benzyloxy)-1-pentyne (1e): ^{1}H NMR δ 7.38−7.27 (m, 5 H), 4.56 (s, 2 H), 3.57 (t, $J = 6.0$ Hz, 2 H), 2.32 (dt, $J = 2.5$ and 7.5 Hz, 2 H), 1.94 (t, $J = 2.5$ Hz, 1 H), 1.83 (quint, $J = 6.5$ Hz, 2 H). IR (neat) 3297, 2951, 2858, 1106, 698 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.330; H, 8.234.

(*Z*)-1-(Tributylstannyl)-1-octene (2a): ^{1}H NMR δ 6.52 (dt, $J = 12.4$ and 7.1 Hz, 1 H), 5.77 (dt, $J = 12.4$ and 1.1 Hz, 1 H, $^2J_{SnH} = 74.4$ Hz), 2.01 (ddt, $J = 6.2$, 7.1 and 1.1 Hz, 2 H), 1.7−1.2 (m, 8 H), 0.92 (t, $J = 7.5$ Hz, 3 H). ^{119}Sn NMR δ −48.8. IR (neat) 2926, 1811, 1465, 665 cm^{-1}. MS (EI) *m/z* (relative intensity) 345 (100, $M^+ - C_4H_9$), 231 (33). Anal. Calcd for $C_{20}H_{42}Sn$: C, 59.87; H, 10.55. Found: C, 60.078; H, 10.353. The chemical shifts of the two olefinic H of **3a** appeared at 5.95 (dt, $J = 19.0$ and 5.0 Hz, 1 H) and 5.84 (d, $J = 19.0$ Hz, 1 H).[3c]

(*Z*)-*β*-(Tributylstannyl)styrene (2b): ^{1}H NMR δ 7.63 (d, $J = 13.4$ Hz, 1 H), 7.35−7.20 (m, 5 H), 6.20 (d, $J = 13.4$ Hz, 1 H, $^2J_{117SnH} = 57.9$ Hz, $^2J_{119SnH} = 55.0$ Hz). IR (neat) 3059, 2957, 1464, 1072, 770, 702 cm^{-1}. MS (EI) *m/z* (relative intensity) 337 (100, $M^+ - C_4H_9$), 223 (45), 197 (17). HRMS (EI) *m/z* calcd for $C_{16}H_{25}Sn$ ($M^+ - C_4H_9$) 337.0978, found 337.1007. The chemical shifts of the two olefinic H of **3b** appeared at 6.87 (s, 2 H).[3c]

(*Z*)-*β*-(Tributylstannyl)-3-methylstyrene (2c): ^{1}H NMR δ 7.58 (d, $J = 7.0$ Hz, 1 H, $^3J_{117SnH} = 129.1$ Hz, $^3J_{119SnH} = 138.9$ Hz), 7.16 (d, $J = 4.1$ Hz, 2 H), 7.11 (d, $J = 4.1$ Hz, 2 H), 6.12 (d, $J = 7.0$ Hz, 1 H, $^2J_{117SnH} = 55.6$ Hz, $^2J_{119SnH} = 58.3$ Hz), 2.33 (s, 3 H). IR (neat) 2957, 1808, 1464, 665 cm^{-1}. MS (EI) *m/z* (relative intensity) 351 (100, $M^+ - C_4H_9$), 237 (42), 211 (29). HRMS (EI) *m/z* calcd for $C_{17}H_{27}Sn$ ($M^+ - C_4H_9$) 351.1135, found 351.1125. The chemical shifts of the two olefinic H of **3c** appeared at 6.85 (d, $J = 19.2$ Hz, 1 H) and 6.77 (d, $J = 19.2$ Hz, 1 H).

(*Z*)-5-(*tert*-Butyldimethylsilyloxy)-1-(tributylstannyl)-1-pentene (2d): ^{1}H NMR δ 6.52 (dt, $J = 12.2$ and 6.9 Hz, 1 H), 5.79 (dt, $J = 12.2$ and 1.1 Hz, 1 H, $^2J_{Sn}H = 72.7$ Hz), 3.62 (t, $J = 6.3$ Hz, 2 H), 2.07 (m, 2H), 1.60 (m, 2H), 0.90 (s, 9 H), 0.05 (s, 6 H). IR (neat) 2929, 1464, 1256, 1104, 836, 775 cm^{-1}. MS (EI) *m/z* (relative intensity) 433 (73, $M^+ - C_4H_9$), 193 (100). HRMS (EI) *m/z* calcd for $C_{19}H_{41}OSiSn$ ($M^+ - C_4H_9$) 433.1949, found 433.1941. The chemical shifts of the two olefinic H of **3d** appeared at 5.96 (dt, $J = 18.8$ and 5.0 Hz, 1 H) and 5.88 (d, $J = 18.8$ Hz, 1 H).

(*Z*)-1-Chloro-1-(tributylstannyl)-1-octene (2f): ^{1}H NMR δ 6.47 (t, $J = 7.7$ Hz, 1 H), 1.98 (dt, $J = 7.7$ and 6.9 Hz, 2 H), 1.60−1.20 (m, 8 H), 1.00−0.80 (m, 3 H). IR (neat) 2927, 1823, 1465 cm^{-1}. MS (EI) *m/z* (relative intensity) 379 (6, $M^+ - C_4H_9$), 269 (100), 267 (76), 265 (40). The chemical shift of the olefinic H of **3f** appeared at 5.77 (t, $J = 7.0$ Hz, 1 H).[3c]

(*Z*)-6-(Tributylstannyl)-6-dodecene (2g): ^{1}H NMR δ 5.97 (t, $J = 7.0$ Hz, 1 H), 2.13 (t, $J = 7.0$ Hz, 2 H), 1.95 (t, $J = 7.0$ Hz, 2H), 1.36−1.25 (m, 18 H), 0.91−0.86 (m, 6 H). IR (neat) 2956, 1465, 665 cm^{-1}. MS (EI) *m/z* (relative intensity) 401 (100, $M^+ - C_4H_9$), 345 (34), 289 (34). The chemical shift of the olefinic H of **3g** appeared at 5.48 (tt, $J = 1.1$ and 6.6 Hz, 1 H).

(*Z*)-α-(Tributylstannyl)stilbene (2h): ^{1}H NMR δ 7.41 (s, 1 H), 7.37−7.12 (m, 10 H). IR (neat) 2954, 762, 698, 665 cm^{-1}. MS (EI) *m/z* (relative intensity) 413 (100, $M^+ - C_4H_9$), 299 (30), 179 (31). HRMS (EI) *m/z* calcd for $C_{22}H_{29}Sn$ ($M^+ - C_4H_9$) 413.1291, found 413.1321. The chemical shift of the olefinic H of **3h** appeared at 6.65 (s, 1 H).

(*Z,Z*)-Bis(1-octenyl)dibutylstannane (4a): ^{1}H NMR δ 6.51 (dt, $J = 12.5$ and 7.0 Hz, 2 H, $^3J_{117SnH} = 147$ Hz, $^3J_{119SnH} = 154$ Hz), 5.81 (dt, $J = 12.5$ and 1.0 Hz, 2 H, $^2J_{117SnH} = 76.6$ Hz, $^2J_{119SnH} = 80.6$ Hz), 2.03 (ddt, $J = 7.0$, 7.0 and 1.0 Hz, 4 H), 1.6−1.2 (m, 24 H), 1.0−0.8 (m, 16 H). IR (neat) 2926, 1599, 1466, 665 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{20}H_{39}Sn$ ($M^+ - C_4H_9$) 399.2072, found 399.2031.

(*Z,Z*)-Bis(3-phenyl-1-propenyl)dibutylstannane (4b): ^{1}H NMR δ 7.38−7.16 (m, 10 H), 6.66 (dt, $J = 12.0$ and 7.0 Hz, 2 H, $^3J_{117SnH} = 115$ Hz, $^3J_{119SnH} = 124$ Hz), 6.02 (dt, $J = 12.0$ and 1.0 Hz, 2 H, $^2J_{117SnH} = 72.0$ Hz, $^2J_{119SnH} = 77.0$ Hz), 3.43 (dd, $J = 1.0$ and 7.0 Hz, 4 H), 1.48 (m, 4 H), 1.35 (m, 4 H), 1.10 (m, 4 H), 0.85 (t, $J = 7.0$ Hz, 6 H). HRMS (EI) *m/z* calcd for $C_{26}H_{36}Sn$ (M^+) 468.1837, found 468.1844, *m/z* calcd for $C_{22}H_{27}Sn$ ($M^+ - C_4H_9$) 411.1133, found 411.1140.

(*Z,Z*)-Bis(3-cyclohexenyl-1-ethenyl)dibutylstannane (4c): ^{1}H NMR δ 6.92 (d, $J = 13.4$ Hz, 2 H), 5.74 (d, $J = 13.4$ Hz, 2 H), 5.67 (dd, $J = 2.7$ and 3.7 Hz, 2 H), 2.15−1.95 (m, 8 H), 1.6−1.2 (m, 16 H), 1.0−0.8 (m, 10H). IR (neat) 2928, 1560, 1447, 665 cm^{-1}. HRMS (EI) *m/z* calcd for $C_{20}H_{31}Sn$ ($M^+ - C_4H_9$) 391.1446, found 391.1436.

Supporting Information Available: Full spectroscopic and analytical characterization of all new compounds (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO952273W