Synthesis, Stereoselective Reactions, and Reactivity of 9-Triptycyldimethyltin Hydride

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*Summary: The synthesis of the new compounds 9-triptycyldimethyltin bromide (**2**) and 9-triptycyldimethyltin hydride (**3**) and some of their physical properties are described. The radical addition of **3** to methyl (E)-2,3-diphenylpropenoate gave the threo adducts as the only products. The results obtained in the addition of hydride **3** to mono- and disubstituted alkynes under radical and palladium-catalyzed conditions indicate that these reactions take place with high stereoselectivity. The chemical reactivity of these vinylstannanes is similar to that of vinyltriorganostannanes containing smaller organic ligands. Full ^1H, ^{13}C, and ^{119}Sn NMR characteristics are included.*

Introduction

In previous studies we have shown that in triorganotin hydrides the size of the organic ligands attached to the tin atom affects not only the reactivity but also the stereoselectivity of the reactions of these hydrides.[1] We have also shown that the vinylstannanes obtained via hydrostannation with tin hydrides containing bulky substituents such as neophyl groups are more stable than their analogues containing less voluminous ligands: such as, for example, *n*-butyl.[2] Following our studies on the synthesis of organotin hydrides containing bulky organic ligands and on the effect of the volume of the substituents on the stereochemistry of hydrostannations, we now wish to report the synthesis of 9-triptycyldimethyltin hydride (**3**) and the results obtained in the hydrostannation of some substituted alkenes and alkynes using this hydride.

Results and Discussion

To obtain 9-triptycyldimethyltin hydride (**3**), we consider it convenient to use 9-triptycyltrimethyltin (**1**) as

Scheme 1. Synthesis of 9-Triptycyldimethyltin Hydride (3)
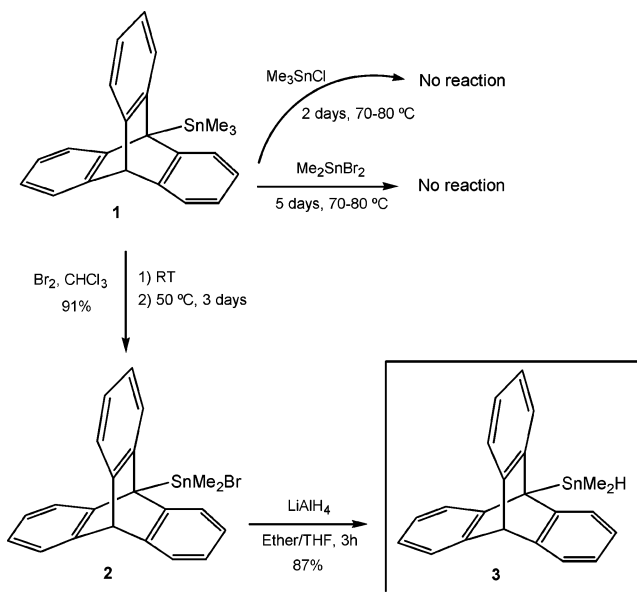
our starting material. In the literature there are some references to the synthesis of **1**,[3,4] as well as of some related 9-triptycyltin derivatives.[5] We repeated these synthetic routes many times, starting from 9-bromoanthracene, always obtaining **1** in very low total yields (8−20%). We were able to improve the yields only up to 25% using a combination of the methods detailed in refs 3 and 4 (see Experimental Section). With **1** as the starting material, 9-triptycyldimethyltin hydride (**3**) was obtained according to Scheme 1.

As shown in Scheme 1, whereas the conversion of **1** into the corresponding bromide **2** is achieved in 91% yield only after 3 days at 50 °C, all attempts made to obtain the corresponding halides by exchange reactions between **1** and both trimethyltin chloride and dimethyltin dibromide failed. These results confirm the low reactivity of the Sn−Me bond when the trimethyltin moiety is attached to the 9-position of tryptycene, as reported by other authors.[3] Reduction of **2** with lithium

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Scheme 2. Addition of 9-Triptycyldimethyltin Hydride (3) to Methyl (E)-2,3-Diphenylpropenoate
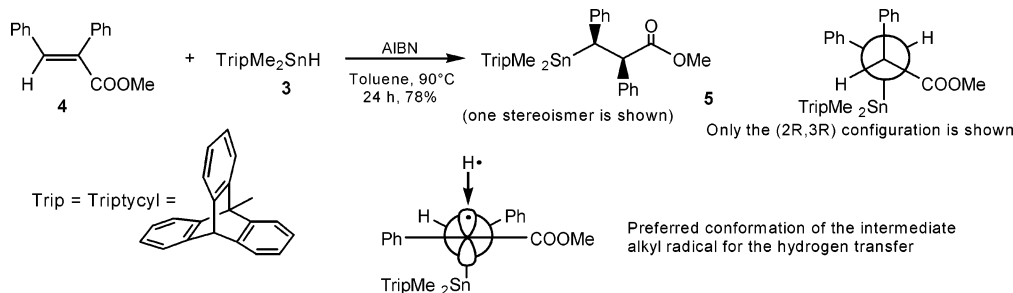
aluminum hydride in diethyl ether/THF led to the solid 9-triptycyldimethyltin hydride (**3**), mp 218−220 °C, in 87% yield.

To determine the stereoselectivities that can be obtained using hydride **3** in the hydrostannation of unsaturated systems, we carried out the addition of this hydride to methyl (*E*)-2,3-diphenylpropenoate (**4**) (Scheme 2) as well as to some terminal and internal alkynes (Tables 1 and 2). The hydrostannation of olefin **4** was carried out under free radical conditions: argon atmosphere, in toluene at 90 °C, using an olefin to **3** ratio of 1:1, and in the presence of azobis(isobutyronitrile) (AIBN), as shown in Scheme 2.

The ^{119}Sn NMR spectrum of the crude product obtained in the addition of hydride **3** to the olefin **4** under free radical conditions showed only one peak at −17.1 ppm, thus indicating the formation of just one of the two possible pairs of diastereoisomers. The ^{13}C NMR chemical shifts (see Experimental Section) corresponding to adduct **5** could easily be assigned through the analysis of the multiplicity of the signals by means of DEPT experiments and taking into account the magnitude of the $^nJ(^{13}C,^{119}Sn)$ coupling constants. The use of the Karplus-type relationship existing[6] between the value of the $^3J(^{13}C,^{119}Sn)$ coupling constants and the dihedral angle, together with ^1H NMR data, enabled us to deduce the stereochemistry of this adduct. Thus, the 8.2 Hz value found for the $^3J(Sn,C=O)$ coupling constant of compound **5** (see Experimental Section) corresponds to a dihedral angle close to 60°.[6b] Similarly, the 42.6 Hz value of the $^3J(Sn-C-C-Ph)$ coupling constant for compound **5** indicates a dihedral angle of about 180° between the triptycyldimethyltin moiety and the phenyl group attached to C-2.

The ^1H NMR spectrum of compound **5** (see Experimental Section) shows $^3J(H,H)$ coupling constants of 9.3 Hz for the protons attached to C-2 and C-3, indicating that these protons are antiperiplanar. The $^3J(Sn-C-C-H)$ coupling constant, with a value of 59.9 Hz, suggests a dihedral angle of approximately 60° between the proton attached to C-2 and the triptycyldimethyltin group.

From the previous discussion, it is possible to attribute a threo configuration, i.e., methyl (2*R*,3*R*)- and (2*S*,3*S*)-2,3-diphenyl-3-triptycyldimethylstannylpropanoates, to the mixture of enantiomeric stereoisomers (**5**). The stereochemistry of this product, obtained from the free radical hydrostannation of olefin **4** with hydride **3**,

(6) (a) Doddrell, D.; Burfitt, I.; Kitching, W.; Lee, C.-H.; Mynott, R. J.; Considine, J. L.; Kuivila, H. G.; Sarma, R. H. *J. Am. Chem. Soc.* **2003**, *68*, 10087. (b) Mitchell, T. N.; Podestá, J. C.; Ayala, A.; Chopa, A. B. *Magn. Reson. Chem.* **1988**, *26*, 497.

Table 1. Triptycyldimethyltin Hydride (3) Radical Additions to Substituted Alkynes[a]
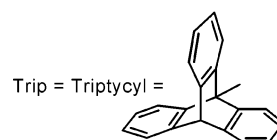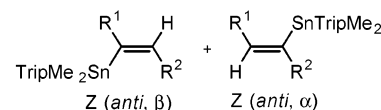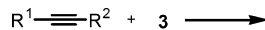
compd	time (h)	temp (°C)	R^1	R^2	(Z)-β (%)	(Z)-α (%)	yield[b] (%)	$^{119}Sn^c$ (ppm)
6	1	60	H	Ph	100		70	−76.9
7, **8**	1	60	H	COOMe	91 (**7**)	9 (**8**)[d,e]	90	−75.1 (**7**), −59.5 (**8**)
9	2	60	COOMe	COOMe	100[f]		89	−58.4
10	3	60	Ph	Ph	100[f]		73	−66.9
11	2	60	Ph	COOMe	100		67	−64.8

[a] Conditions: reactions carried out under an argon atmosphere; hydride to alkyne ratio 1:1; AIBN 0.01 equiv; without solvent. [b] Yields of products isolated from chromatography. [c] In CDCl$_3$; in ppm with respect to Me$_4$Sn. [d] From the ^1H and ^{119}Sn NMR spectra. [e] In this case isomer α. [f] In these cases (Z)-β = (Z)-α.

is in agreement with what was expected when taking into account the nature of the substituents attached to C-2 of the starting olefin, as demonstrated in previous studies (see Scheme 2).[1e] The complete diastereoselectivity observed suggests that the steric volume of the triptycyldimethyltin group has a greater effect on the stereochemistry than that of other triorganotin moieties used in similar studies carried out previously.[1]
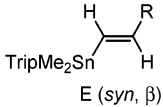
We then studied the hydrostannation of various terminal and internal alkynes with triptycyldimethyltin hydride (**3**). We first carried out the addition of hydride **3** under the free radical conditions of argon atmosphere, AIBN, without solvent, and 60 °C to phenyl- and diphenylethyne, methyl propiolate, methyl 3-phenylpropiolate, and dimethyl acetylenedicarboxylate. The results obtained are summarized in Table 1.

This table shows that the addition of triptycyldimethyltin hydride (**3**) leads in all cases exclusively to the (*Z*)-vinylstannanes resulting from an anti attack, this demonstrating the high stereoselectivity that can be achieved using hydride **3**. The *Z* geometry of compounds **6**−**11** was assigned by taking into account that the large $^3J(Sn,H)$ coupling constants observed (Supporting Information), all of them over 100 Hz, indicate the existence of trans H−C−C−Sn linkages in these vinylstannanes. Other ^1H and ^{13}C NMR data (Supporting Information) also confirmed the assigned structures.
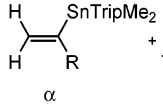
Table 2. Triptycyldimethyltin Hydride (3) Palladium-Catalyzed Additions to Substituted Alkynes[a]
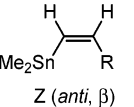
H—≡—R + 3 ⟶

		E (*syn*, β)		α		Z (*anti*, β)	

compd	time (h)	temp (°C)	R	(E)-β (%)	α (%)	(Z)-β (%)	yield[b] (%)	^{119}Sn[c] (ppm)
12, 13	2	25	Ph	70 (**12**)	30 (**13**)		85[d]	−57.4 (**12**), −57.6 (**13**)
8, 7	2	25	COOMe		89 (**8**)	11 (**7**)	90	−59.5 (**8**), −75.1 (**7**)
14, 15	2	25	CH$_2$OH	67 (**14**)	33 (**15**)		80	−60.4 (**14**), −62.9 (**15**)

[a] Conditions: reactions carried out under an argon atmosphere; hydride to alkyne ratio 1:1; (PPh$_3$)$_2$PdCl$_2$ 2% in THF. [b] Yields of products isolated from chromatography, except when otherwise stated. [c] In CDCl$_3$; in ppm with respect to Me$_4$Sn. [d] Could not be separated by chromatography; ratio obtained from the ^{1}H and ^{119}Sn NMR spectra.

These results are in agreement with those reported previously for the addition of trineophyltin hydride to the same alkynes.[1f]

It should be mentioned that all the attempts we made to add hydride **3** to propargyl alcohol under radical conditions were unsuccessful.

On the other hand, the addition of **3** catalyzed by bis-(triphenylphosphine)palladium(II) chloride to phenylethyne, methyl propiolate, and propargyl alcohol also takes place stereoselectively, leading in most cases to the products of a syn attack, mainly as a mixture of the two possible regioisomers in very good yields (Table 2). The stereochemistry of adducts **12−15** was assigned by taking into account that the observed ^3J(Sn,H) coupling constants were in the range of 70−76 Hz, clearly indicating a cis arrangement of the proton attached to vinyl carbon 2 and the triptycyldimethyltin moiety attached to vinyl carbon 1 in these vinylstannanes. Other ^{1}H and ^{13}C NMR data confirmed the assigned structures.

It should be noted that in this case the addition of **3** to methyl propenoate leads to a mixture of the same products obtained in the hydrostannation under radical conditions (see Table 1, compounds **7** and **8**), but now in a completely opposite ratio: 89% of **8** and 11% of **7** (Table 2). Another unusual feature of this reaction was the formation of **7**: i.e., the product corresponding to an anti addition under palladium-catalyzed conditions.[1f]

We found that the chemical reactivity of the new vinylstannanes is similar to that of other vinyltriorganostannanes. Thus, as shown in Scheme 3, the Stille reaction of methyl 2-triptycyldimethylstannylpropenoate (**8**) with bromobenzene gives methyl 2-phenylpropenoate (**16**) in 65% yield[7,8] and the iododestannylation of (Z)-1-triptycyldimethylstannyl-1,2-diphenylethene (**10**) leads quantitatively to the corresponding (Z)-1-iodo-1,2-diphenylethene (**17**).

To estimate the relative reactivity of organotin hydrides, we are at present using a method based upon

Scheme 3. Reaction of Vinylstannanes with Bromobencene and Iodine
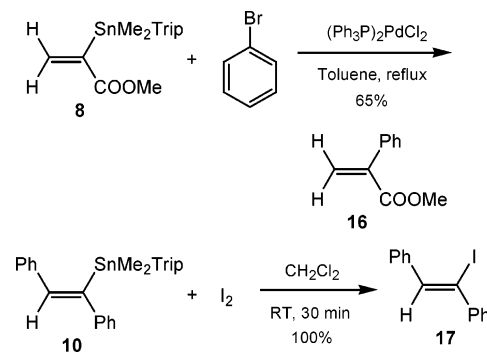
the study of the composition of the mixture of products resulting from the reaction of organotin hydrides with 6-bromo-1-hexene under radical conditions, which will be reported in a publication soon. The current study has demonstrated that a tin hydride with bulky organic ligands such as trineophyltin hydride can effect hydrogen transfer to the intermediate alkyl radicals more quickly than does triptycyldimethyltin hydride (**3**), showing the great effect upon the reactivity obtained by, for example, replacing one small organic ligand such as the methyl group of the trimethyltin hydride by the bulkier triptycyl ligand.

Experimental Section

NMR spectra were obtained using a Bruker ARX 300 instrument. Mass spectra were obtained using a Finnigan MAT Model 8230 instrument at Dortmund University (Germany). Elemental analyses (C, H) were carried out with a Carlo Erba Instrument at Santiago de Compostela University (Spain). The melting points were determined with a Kofler hot stage apparatus and are uncorrected. All the solvents and reagents used were of analytical reagent grade. Dimethyl acetylenedicarboxylate and methyl 3-phenylpropiolate were obtained by following known techniques.[9-11] 9-Bromotriptycene was obtained in 45% yield according to known procedures.[12]

Synthesis of 9-Triptycyltrimethyltin (1). *n*-Butyllithium (38.0 mL, 1.36 M, 54 mmol in hexane) was added dropwise to a fine suspension of 9-bromotriptycene (8.80 g, 26.3 mmol) in dry diethyl ether (150 mL) with vigorous stirring in an argon atmosphere. The mixture was stirred for 3 h. Then, a solution of trimethyltin chloride (5.20 g, 26 mmol) in dry diethyl ether (100 mL) was added. The mixture was heated under reflux for 2 h and then left overnight at room temperature with stirring. Distilled water (75 mL) was added cautiously, followed by benzene (400 mL). The mixture was filtered to remove some insoluble material and the organic phase of the filtrate separated, washed with water, and dried over magnesium sulfate to give a white solid. This was recrystallized twice from cyclohexane to give **1**: mp 294−295 °C (lit.[3] idem); yield 6.13 g (14.72 mmol, 56%).

Synthesis of 9-Triptycyldimethyltin Bromide (2). To a solution of 9-triptycyltrimethyltin (**1**; 1.00 g, 2.40 mmol) in chloroform (5 mL) under argon, at room temperature, was added dropwise with stirring a solution of bromine (0.38 g, 2.40 mmol) in chloroform (5 mL). The mixture was stirred for 3 days at 40−50 °C and monitored by ^{1}H NMR until disap-

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(8) Hageman, H. J. *Eur. Polym. J.* **1999**, 35, 991

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(10) (a) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, 13, 317. (b) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, 24, 553.

(11) Huntress, E. H.; Lesslie, T. E.; Bornstein, J. *Org. Synth.* **1952**,32, 55.

(12) *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longman: London, 1978; p 609.

pearance of compound **1**. The solvent was removed under reduced pressure, and the crude product was recrystallized in cyclohexane at 40 °C (the compound is sensitive to temperature), affording a white crystalline solid: mp 279−281 °C; yield 1.05 g (2.18 mmol, 91%). ^{1}H NMR (CDCl$_3$): δ 1.17 (s, 6H, ^2J(Sn,H) = 53.8 Hz); 5.31 (s, 1H); 6.83−7.46 (m, 12H). ^{13}C NMR (CDCl$_3$): δ 1.08 (^1J(Sn,C) = 357.2 Hz); 58.17 (^1J(Sn,C) = 358.6 Hz); 54.46; 123.48; 124.23; 124.97; 125.43; 146.24; 147.13. ^{119}Sn NMR (CDCl$_3$): δ 84.9.

Synthesis of 9-Triptycyldimethyltin Hydride (3). To a suspension of LiAlH$_4$ (0.20 g, 4.97 mmol) in dry diethyl ether (10 mL) under an atmosphere of argon at room temperature was added dropwise a solution of 9-triptycyldimethyltin bromide (**2**; 2.00 g, 4.14 mmol) in THF (60 mL). The mixture was heated under reflux for 3 h. THF was evaporated and replaced by diethyl ether, and then a saturated solution of NH$_4$Cl was added. The organic layer was separated, and the aqueous layer was extracted three times with diethyl ether. The combined organic extracts were dried over anhydrous MgSO$_4$. Removal of the solvent under reduced pressure gave **3**: mp 218−220 °C; yield 1.45 g (3.59 mmol, 87%). ^{1}H NMR (CDCl$_3$): δ 0.57 (s, 6H, ^2J(Sn,H) = 53.0 Hz); 5.27 (s, 1H); 5.80 (m, 1H, ^1J(^{119}Sn,^{1}H) = 1804.0 Hz); 6.73−7.47 (m, 12H). ^{13}C NMR (CDCl$_3$): δ −9.96 (^1J(Sn,C) = 357.2 Hz); 67.46; 55.13; 123.98; 124.87; 125.02; 125.26; 147.91; 148.52. ^{119}Sn NMR (CDCl$_3$): δ −128.5.

Synthesis of Methyl (2R,3S)- and (2S,3R)-2,3-diphenyl-3-triptycyldimethylstannylpropanoate (5). To a solution of hydride **3** (0.38 g, 0.94 mmol) in dry toluene (1 mL) was added a solution of methyl (*E*)-2,3-diphenylpropenoate (**4**; 0.22 g, 0.94 mmol) in toluene (1 mL) and a catalytic amount of AIBN. The mixture was stirred for 24 h at 90 °C under an argon atmosphere. The reaction was monitored by taking samples at intervals and observing the disappearance of the Sn−H absorption by IR. Then the solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel 60). Compound **5** was isolated in the fraction eluted with hexane−diethyl ether (98: 2): mp 221−223 °C; yield 0.47 g (0.73 mmol, 78%). ^{1}H NMR (CDCl$_3$): δ 0.52 (s, 3H, ^2J(Sn,H) = 49.6 Hz); 0.58 (s, 3H, ^2J(Sn,H) = 49.6 Hz); 3.57 (s, 3H); 3.87 (d, 1H, ^3J(H,H) = 9.3, ^2J(Sn,H) = 59.9 Hz); 4.50 (d, 1H, ^3J(H,H) = 9.3, ^3J(Sn,H) = 59.9 Hz); 5.18 (s, 1H); 6.61−7.41 (m, 22H). ^{13}C NMR (CDCl$_3$): δ −6.13 (^1J(Sn,C) = 329.7 Hz); −4.23 (^1J(Sn,C) = 307.5 Hz); 39.91 (^1J(Sn,C) = 331.7 Hz); 52.49; 55.19 (^2J(Sn,C) = 16.0 Hz); 55.57; 57.69 (^1J(Sn,C) = 377.7 Hz); 123.87; 124.83; 125.09; 127.23; 128.38; 128.45; 128.70; 129.12 (^3J(Sn,C) = 23.9 Hz); 139.07 (^3J(Sn,C) = 42.6 Hz); 142.94 (^2J(Sn,C) = 28.5 Hz); 147.72; 175.13 (^3J(Sn,C=O) = 8.2 Hz).

Addition of 9-Triptycyldimethyltin Hydride (3) to Substituted Alkynes under Radical Conditions. Typical Procedure. A mixture of phenylethyne (0.076 g, 0.74 mmol), hydride **3** (0.30 g, 0.74 mmol), and AIBN as a catalyst was heated under argon at 60 °C for 1 h (this optimal time of reaction and temperature was indicated by earlier experiments, in which the reaction was monitored by taking samples at intervals and observing the disappearance of the Sn−H absorption by IR). The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra of the crude product showed that it consisted of isomer (*Z*)-**6** only. Column chromatography (silica gel 60) of this product afforded compound **6** (0.26 g, 0.52 mmol, 70%) in the fraction eluted with hexane−diethyl ether (99:1): mp 153−155 °C. NMR spectra, physical characteristics, and other analytical data of

6 and adducts **7**−**11** are included in the Supporting Information.

Addition of 9-Triptycyldimethyltin Hydride (3) to Substituted Alkynes Catalyzed by Bis(triphenylphosphine)palladium(II) Chloride. Typical Procedure. To a solution of propargyl alcohol (0.047 g, 0.80 mmol) and bis-(triphenylphosphine)palladium(II) chloride (0.010 g, 0.018 mmol) in dry THF (3 mL) under argon was added hydride **3** (0.34 g, 0.80 mmol), and the mixture was stirred at room temperature for 2 h. Then, the solvent was distilled off under reduced pressure. The ^{119}Sn NMR spectrum of the crude product showed a mixture of two compounds: (*E*)-β-3-triptycyldimethylstannyl-2-propen-1-ol (**14**; 67%) and α-2-triptycyldimethylstannyl-2-propen-1-ol (**15**; 33%). Column chromatography (silica gel 60) of the mixture afforded **14** (yield 0.19 g (0.41 mmol, 52%): mp 70−72 °C) and **15** (yield 0.10 g (0.22 mmol, 28%); mp 174−176 °C) in the fractions eluted with 96:4 and 93:7 hexane−diethyl ether, respectively. NMR spectra, physical characteristics, and other analytical data of adducts **12**−**15** are included in the Supporting Information.

Stille Coupling Reaction: Synthesis of Methyl 2-Phenylpropenoate (16). To a mixture of bromobenzene (0.12 g, 0.74 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.011 g, 2%), and some crystals of 2,6-di-*tert*-butyl-4-methylphenol under argon was added a solution of **8** (0.39 g, 0.81 mmol) in dry toluene (2 mL) at room temperature, and this mixture was stirred for 24 h under reflux, with monitoring by TLC. Column chromatography on silica gel 60 of the crude product gave compound **16** (0.079 g, 0.48 mmol, 65%)[7,8] in the fraction eluted with 98:2 hexane−diethyl ether.

Iododestannylation Reaction: Synthesis of (Z)-1-Iodo-1,2-diphenylethene (17). To a solution of **10** (0.24 g, 0.41 mmol) in dry CH$_2$Cl$_2$ (4.5 mL) under argon was added iodine (0.12 g, 0.45 mmol). The mixture was stirred at room temperature for 30 min, with monitoring of the reaction by TLC. Column chromatography on silica gel 60 of the crude product gave iodovinyl compound **17** in the fraction eluted with hexane: yield 0.12 g (quantitative); mp 136−138 °C. ^{1}H NMR (CDCl$_3$): δ 7.27−7.82 (m). ^{13}C NMR (CDCl$_3$): δ 102.02; 126.04; 126.17; 126.68; 126.96; 127.41; 127.69; 134.98; 138.24; 138.77.

Supporting Information Available: Characterization data for the products including full ^{1}H (Table 3) and ^{13}C NMR spectra (Table 4), as well as mass spectra and elemental analyses of the isolated pure compounds. This material is available free of charge via the Internet at http://pubs.acs.org.