Palladium- and Molybdenum-Catalyzed Hydrostannation of Alkynes. A Novel Access to Regio- and Stereodefined Vinylstannanes

H. X. Zhang, F. Guibé,* and G. Balavoine

Institut de Chimie Moléculaire d'Orsay, Laboratoire de Chimie Organique des Elêments de Transition, URA, DO 255-CNRS, Bât 420, 91405 ORSAY Cedex, France

Received April 4, 1989

In the presence of catalytic amounts of dichlorobis(triphenylphosphine)palladium or of the π-allylmolybdenum complex **3**, tributyltin hydride adds instantaneously at room temperature to various alkynes to give the corresponding vinylstannanes in good to excellent yields. The reaction is totally stereoselective (cis addition). With monoalkylacetylenes RC≡CH, good regioselectivity for the formation of 1-(tributylstannyl)alkenes (vs 2-(tributylstannyl)alkenes) is attained only if the R substituent is sufficiently bulky. The molybdenum-catalyzed hydrostannation of (trimethylsilyl)acetylene gives 1-(tributylstannyl)-1-(trimethylsilyl)ethene with 85% selectivity. The palladium-catalyzed hydrostannation of 1-chloro-1-octyne regio- and stereoselectively yields (*E*)-1-chloro-1-(tributylstannyl)octene, which, on reaction with I_2 or Br_2, leads to the corresponding 1-chloro-1-halo-1-octenes with total conservation of stereochemistry. 1-Bromo-1-alkynes behave differently from their chloro analoguers, reacting with 2 equiv of tributyltin hydride to give (*E*)-1-(tributylstannyl)-1-alkenes. Conjugated alkynones or alkynoic esters generally yield (*E*)-α-(tributylstannyl)enones and enoates esters which are important synthons in organic chemistry. Symmetrically substituted internal conjugated diynes, 1,3-diynes and 1-(trimethylsilyl)-1,3-diynes give a single monohydrostannation product with total chemo-, regio-, and stereoselectivity.

Introduction

Vinylstannanes which can lead to carbon–carbon bond formation under a variety of conditions are of increasing importance as intermediates in synthetic organic chemistry.[1]

Indeed, vinylstannanes can be condensed with a large array of electrophiles including carbonyl compounds, enones, acyl chlorides, vinyl, aryl, allyl, and benzyl halides or triflates. In these reactions, vinylstannanes may be used as they are, in conjunction with palladium catalysts,[1,2] or following prior in situ conversion to some other organometallic species (usually the vinyllithium or vinylcopper (I)).[1,3,4] Carbon–carbon bond formation under free-radical conditions has also been reported and used for synthetic purposes.[5] Recently copper(II) nitrate mediated coupling of alkenylstannanes, leading to symmetrically substituted 1,3-dienes, has been described.[6] Except for the radical reactions, all of the above-mentioned carbon–carbon bond formation reactions generally proceed with retention of the double bond geometry of the starting vinylstannane. Palladium-catalyzed reactions, copper(II)-mediated coupling reactions, and radical reactions are carried out under very mild conditions and therefore tolerate the presence of a wide variety of functional groups.

Due to their great versatility as building blocks for synthesis, considerable effort has been devoted, especially in recent years, to the regio- and stereocontrolled synthesis of vinylstannanes.[1,4] Among the existing routes, the addition of tin compounds to acetylenic bonds appears to be one of the most straightforward methods. Following the pioneering work of Leusink, Noltes and co-workers,[7] radical tin hydride addition to acetylenic bonds has been extensively used.[8] Recently, the direct or transition metal catalyzed additions of various metal or metalloid tin derivatives (that is, species containing Sn–Cu[9–11] Sn–Zn,[10] Sn–Mn,[10] Sn–B,[10,12] Sn–Al,[10] Sn–Mg,[10] Sn–Si,[13,14] Sn–Ge,[15] or Sn–Sn[16] bonds) were studied by several groups. Rather surprisingly, however, the transition metal catalyzed addition of tin hydrides to acetylenic compounds has seldom been considered.[17] In this paper, we report our results

(1) Leading references: (a) Pereyre, M.; Quintard, J. P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1986. (b) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (c) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

(2) Electrophiles used in palladium-catalyzed condensation reactions[1b,c] include acyl chlorides, allyl halides, vinyl halides and triflates, aryl halides and triflates, vinyl epoxides and perfluoroalkyl iodides. For very recent references, see the following. Vinyl halides: (a) Stille, J. K.; Groh, B. L. *J. Am. Chem. Soc.* **1987**, *109*, 813. Aryl halides: (b) McKean, D. R.; Parinello, G.; Renaldo, A. F.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 422. (c) Haack, R. A.; Penning, T. D.; Djuric, S. W.; Dziuba, J. A. *Tetrahedron Lett.* **1988**, *29*, 2783. (d) Piers, E.; Lu, Y. F. *J. Org. Chem.* **1988**, *53*, 926. Aryl triflates: (e) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. Vinyl triflate: (f) Scott, W. J.; Mc Murry, J. E. *Acc. Chem. Res.* **1988**, *21*, 47. (g) Stille, J. K.; Tanaka, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 3785. (h) Peña, M. R.; Stille, J. K. *Tetrahedron Lett.* **1987**, *28*, 6573. (i) Krolski, M. E.; Renaldo, A. F.; Rudisil, D. E.; Stille, J. K. *J. Org. Chem.* **1988**, *53*, 1170. Vinyl epoxides: (j) Echavarren, A. M.; Tueting, D. R.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *110*, 4039. Allyl halides: (k) Carola Acuña, A.; Zapata, A. *Synth. Commun.* **1988**, *18*, 1125. Acyl chlorides: (l) Carola Acuña, A.; Zapata, A. *Synth. Commun.* **1988**, *18*, 1133. Perfluoroalkyl iodides: (m) Matsubara, S.; Mitani, M.; Utimoto, K. *Tetrahedron Lett.* **1987**, *28*, 5857.

(3) Behling, J. R.; Babiak, K. A.; Ng, J. S.; Campbell, A. L.; Moretti, R.; Koerner, M.; Lipshutz, H. B. *J. Am. Chem. Soc.* **1988**, *110*, 2641.

(4) Wulff, W. D.; Peterson, G. A.; Bauta, E. W.; Chan, K. S.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem.* **1986**, *51*, 277 and references therein.

(5) (a) Baldwin, J. E.; Kelly, D. R.; Ziegler, C. B. *J. Chem. Soc., Chem. Commun.* **1984**, 133. (b) Baldwin, J. E.; Kelly, D. R. *J. Chem. Soc., Chem. Commun.* **1985**, 682. (c) Harris, F. L.; Weiler, L. *Tetrahedron Lett.* **1987**, *28*, 2941.

(6) Ghozal, S.; Luke, J. P.; Kyler, K. S. *J. Org. Chem.* **1987**, *52*, 4296.

(7) Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1968**, *11*, 541 and references therein.

(8) See for instance: (a) Nativi, C.; Taddei, M. *J. Org. Chem.* **1988**, *53*, 820. (b) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547. (c) Ensley, H. E.; Buescher, R. R.; Lee, K. *J. Org. Chem.* **1982**, *47*, 404. (d) Jung, M. E.; Light, L. A. *Tetrahedron Lett.* **1982**, *23*, 3851. (e) Corey, E. J.; Wollenberg, R. H. *J. Org. Chem.* **1975**, *40*, 2265.

(9) Zweifel, G.; Leong, W. *J. Am. Chem. Soc.* **1987**, *109*, 6409.

(10) Sharma, S.; Oehlschlager, A. C. *Tetrahedron Lett.* **1986**, *27*, 6161 and references therein.

(11) Piers, E.; Tillyer, R. D. *J. Org. Chem.* **1988**, *53*, 5366 and references therein.

(12) Sharma, S.; Oehlschlager, A. C. *Tetrahedron Lett.* **1988**, *29*, 261.

(13) Mitchell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schneider, U. *J. Org. Chem.* **1987**, *52*, 4868.

(14) Chdnard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561.

(15) Piers, E.; Skerlj, R. T. *J. Chem. Soc., Chem. Commun.* **1987**, 1025.

(16) Piers, E.; Skerlj, R. T. *J. Chem. Soc., Chem. Commun.* **1986**, 626 and references therein. See also Note Added in Proof.

(17) After this work was well underway, two short communications appeared dealing, respectively, with palladium-catalyzed and with rhodium-catalyzed hydrostannation reactions: (a) Ichinose, Y.; Oda, H.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3468. (b) Kikuhawa, K.; Umekawa, F.; Wada, G.; Matsuda, T. *Chem. Lett.* **1988**, 881.

0022-3263/90/1955-1857$02.50/0

Table I. Palladium- and Molybdenum-Catalyzed Hydrostannation of Monoalkyl-Substituted Acetylenes

entry	R in R—≡—H 7	catalyst [M]	$H_2C{=}C(R)SnBu_3$ 8 (α)	$Bu_3Sn(H)C{=}C(R)H$ 9 (β-*E*)	isolated yield,[a] %
a	CH_2OH (**7a**)	Pd	**8a**/**9a** (55/45)		41[b]
		Mo	**8a**/**9a** (67/33)		–[d]
b	CH_2OPh (**7b**)	Pd	**8b**/**9b** (91/9)		85[b]
		Mo	**8b**/**9b** (74/26)		–[d]
c	CH_2OTHP (**7c**)	Pd	**8c**/**9c** (67/33)		68
		Mo	**8c**/**9c** (64/36)		–[d]
d	CH_2NMe_2 (**7d**)	Pd	**8d**/**9d** (32/68)		60[b]
		Mo	no reaction[c]		
e	$CH(OH)CH_3$ (**7e**)	Pd	**8e**/**9e** (20/80)		–[d]
f	$C(CH_3)_2OH$ (**7f**)	Pd	**8f**/**9f** (0/100)		85
		Mo	**8f**/**9f** (53/47)		–[d]
g	$CH(OH)$-*n*-C_5H_{11} (**7g**)	Pd	**8g**/**9g** (25/75)		–[d]
		Mo	**8g**/**9g** (56/44)		67[b]
h	$CH(n\text{-}C_5H_{11})OTBS$[e]	Pd	**8h**/**9h** (28/72)		94[b]
		Mo	**8h**/**9h** (73/27)		94[b]
i	CH(OH)Ph (**7i**)	Pd	**8i**/**9i** (24/76)		–[d]
j	*n*-C_6H_{13} (**7j**)	Pd	**8j**/**9j** (57/43)		–[d]
		Mo	**8j**/**9j** (50/50)		–[d]
k	*n*-C_4H_9 (**7k**)	Pd	**8k**/**9k** (35/65)		98[b]
l	$CH(n\text{-}C_5H_{11})_2$ (**7l**)	Pd	**8l**/**9l** (0/100)		90
		Mo	**8l**/**9l** (58/42)		89[b]

[a] Analytical yields were always nearly quantitative; loss of material during chromatographic purification is mainly the result of silica-induced protodestannylation. [b] Isolated as a mixture of regioisomers. [c] Probably due to inactivation of the catalyst by the dimethylamino group. [d] The products were not isolated. [e] TBS = *tert*-butyldimethylsilyl.

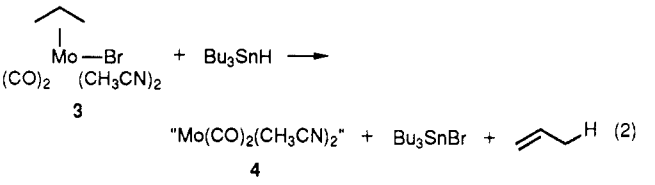
in this area. The particular case of the reductive cleavage of propargylic halides and esters will be dealt with in a further publication. A preliminary account of these works has already been published.[18,19]

General Procedure for Catalytic Hydrostannation of Acetylenic Compounds with Tributyltin Hydride

In this work, both palladium and molybdenum catalysts were considered. The palladium catalyst was the dichlorobis(triphenylphosphine)palladium(II) complex **1**. This air-stable compound, which is very easily prepared, had already been found to efficiently catalyze the hydrostannolysis of acyl chlorides and allylic esters and the hydrostannation of enones.[19] The true catalytic species in these reactions is thought to be the coordinatively unsaturated bis(triphenylphosphine)palladium(0) **2**, which forms in situ upon reduction of **1** by tributyltin hydride (eq 1). Palladium-catalyzed hydrostannation of alkynes may be carried out in various solvents, such as dichloromethane, benzene, or THF.

$$\underset{\mathbf{1}}{PdCl_2(PPh_3)_2} + 2Bu_3SnH \rightarrow \underset{\mathbf{2}}{Pd(PPh_3)_2} + H_2 + 2Bu_3SnCl \quad (1)$$

We later discovered that the bromo π-allyl complex of molybdenum **3**[20] was also an efficient hydrostannation catalyst; **3** may even be superior to **1** in the cases of certain deactivated or sterically hindered alkynes (vide infra). With **3**, it is imperative that the reaction be performed in a good solvating solvent such as THF. In this case as well, the true catalytic species is probably a zero-valent metal entity such as **4**, formed in situ through reduction by tributyltin hydride (eq 2). Solvation by THF, together with coordination to the alkyne, would then be necessary to insure sufficient stabilization of the Mo(0) entity.[21]



Typically, transition metal catalyzed hydrostannations of alkynes were carried out at room temperature and under an inert atmosphere by adding tributyltin hydride (1.1–1.2 equiv) dropwise over a period of a few minutes to a solution (approximately 0.5 M) of the alkyne in the presence of the catalyst (usually 2×10^{-2} equiv of **2** or 4×10^{-2} equiv of **3**). The reactions are slightly exothermic and are usually complete within a few minutes. Due to the presence of the transition metal catalyst, any excess of tributyltin hydride is rapidly decomposed, forming hexabutyldistannane and hydrogen according to eq 3.[19b]

$$2Bu_3SnH \xrightarrow{M_T} H_2 + Bu_3SnSnBu_3 \quad (3)$$

The reactions are conveniently monitored by NMR spectroscopy and, for monosubstituted acetylenic compounds, by IR spectroscopy (disappearance of the C–H acetylenic band at ca. 3300 cm^{-1}). Completion of reaction is usually signaled by a sudden and typical darkening of

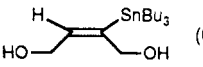
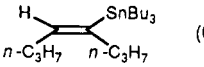
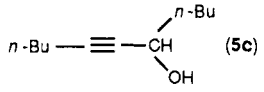
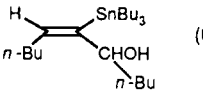
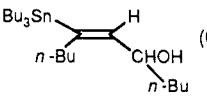
(18) Zhang, H. X.; Guibé, F.; Balavoine, G. *Tetrahedron Lett.* **1988**, *29*, 619, 623. Corrigendum: *Tetrahedron Lett.* **1988**, *29*, 3874.

(19) Previous studies on palladium-catalyzed hydrostannolytic or hydrostannation reactions: (a) Guibé, F.; Zigna, A. M.; Balavoine, G. *J. Organomet. Chem.* **1986**, *306*, 257. (b) Dangles, O.; Guibé, F.; Balavoine, G.; Lavielle, S.; Marquet, A. *J. Org. Chem.* **1987**, *52*, 4984 and references therein.

(20) Tom Dieck, H.; Friedel, H. *J. Organomet. Chem.* **1968**, *14*, 375.

(21) In the absence of acetylenic compounds, an orange solution of **3** in THF under argon atmosphere immediately turns black and cloudy upon addition of Bu_3SnH. NMR analysis (THF-d_6) shows a complete disappearance of the proton signals[20] of the π-allyl entity. The tin byproduct of the reaction is Bu_3SnBr (GC/MS). IR analysis (after dilution in $CHCl_3$) shows a single strong CO absorption at 1950 cm^{-1}. Thus, the species which forms is not the known $(THF)_3Mo(CO)_3$ (ν_{CO} = 1920 and 1780 cm^{-1}. Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 201). If the reaction of **3** and Bu_3SnH is performed under CO atmosphere (in this case the solution turns red and stays homogeneous), the CO band at 1950 cm^{-1} is progressively replaced, over ca. 1 h, by the CO band at 1986 cm^{-1} of $Mo(CO)_6$, which can be precipitated out of the solution quantitatively.

Table II. Palladium- and Molybdenum-Catalyzed Hydrostannation of Dialkyl-Substituted Acetylenes

starting alkyne	catalyst	product	isolated yield, %
$HOCH_2CH{\equiv}CHCH_2OH$ (**5a**)	Pd	 (**6a**)	92
n-$C_3H_7C{\equiv}C$-n-C_3H_7 (**5b**)	Pd	 (**6b**)	11[a]
	Mo		95
 (**5c**)	Pd	 (**6ca**) +  (**6cb**)	65[b]

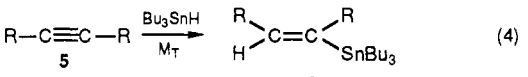
[a] Analytical yield. Most of the alkyne was recovered at the end of the reaction. [b] Mixture of regioisomers (**6ca**/**6cb** = 33/67); about 20% of **5c** was left unreacted.

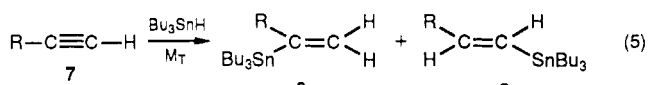
the solution and by some hydrogen gas evolution (eq 3).

Results

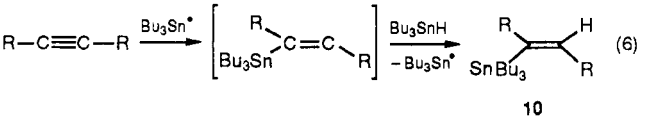
A. Catalytic Hydrostannation of Simple Mono- or Disubstituted Acetylenic Compounds. The results obtained in the catalytic hydrostannation reactions (eq 4 and 5), in THF, of simple mono- and disubstituted alkynes are collected in Tables I and II. The regio- and stereochemical structures of the vinylstannanes were deduced without ambiguity from NMR data, especially from the chemical shifts and coupling patterns J_{HH}, $J(^{117}SnH)$, $J(^{119}SnH)$ of vinylic protons.[8d,22] The isomer ratio for a given reaction was initially deduced from NMR data on the crude reaction mixture and subsequently corroborated by capillary GC analysis. Unless otherwise noted, conversion of starting material was always total, and analytical yields (determined by NMR with anisole as the internal reference) were greater than 90%. Isolation of products, which was systematically carried out when good regio- and stereoselectivities were observed, simply involved short column chromatography on silica. Some loss of product was observed from time to time during chromatographic purification, mainly as a result of silica-induced protolytic cleavage of the tin–carbon bond.[23]

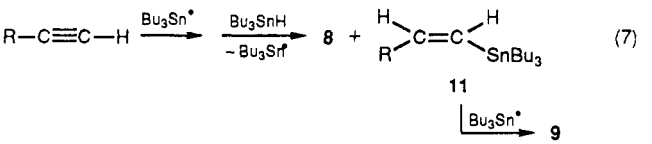
Inspection of Table I shows that the results of catalytic hydrostannation reactions differ widely from those of radical-induced reactions. As was expected, the palladium- and molybdenum-catalyzed hydrostannation reactions are syn additions, leading to vinylstannanes of exclusively E configuration, i.e. **6** (eq 4) or **9** (eq 5).


(4)


(5)

A similar stereospecificity is observed in the rhodium-catalyzed hydrostannation of terminal alkynes.[17b] In contrast, radical additions are known to take place trans to the triple bond, to give the Z isomers **10** or **11** as the primary adducts[7] (eq 6 and 7). The Z isomer **11** may then isomerize, especially in the presence of tin radicals,[7,8a] to the more stable E isomer **9**. Therefore, the stereochemistry of radical hydrostannation reactions may be difficult to control.[8a]


(6)


(7)

Unlike the stereochemistry, the regiochemistry of palladium- or molybdenum-catalyzed hydrostannation reactions is not clear-cut. Terminal acetylenes usually give a mixture of regioisomers α, **8** (stannyl group α to the R substituent), and β-(E), **9**. Radical hydrostannations also usually give a mixture of regioisomers of α and β-(E + Z) but, in general, discrimination between the substituted and unsubstituted carbon atoms of the triple bond is more pronounced in radical reactions. For example, radical tributyltin hydride hydrostannation of propargyl alcohol and its benzyl or THP derivatives gives the β-adduct with selectivities 84%,[8d] 93%,[8d] and 100%,[8e] respectively. Radical-initiated addition of triethyltin hydride on 1-hexyne gives the β-adduct with 97% selectivity.[22,24] All of these values may be compared with the more balanced results of Table I (entries a, c, d, j, k). Branching of the carbon next to the triple bond favors the formation of the β-adduct **9**, as can be seen with simple alkyl-substituted alkynes (entries j–l), as well as in the series of substituted propargylic alcohols (entries a, e, f, i,). Total regioselectivity toward the formation of the β-regioisomer is obtained with 3-pentyl-1-octyne **7l**, which bears a secondary substituent on the acetylenic bond, and with the tertiary alcohol **7h**. In the case of the secondary propargyl alcohol, 1-octyn-3-ol, increasing the steric bulk of the substituent through O-*tert*-butyldimethylsilylation does not improve the regioselectivity (entries g and h). The unexpectedly good selectivity toward the formation of the α-isomer **8b** from the phenyl ether **7b** (propargyl phenoxide) is worthy of note.

For a given substrate, the palladium and the molybdenum catalysts lead to different regiochemistries. In particular, with sterically hindered substrates, the molybdenum catalyst systematically favors the formation of the

(22) Leusink, A. J.; Budding, H. A. J.; Marsman, J. W. *J. Organomet. Chem.* **1967**, *9*, 285.
(23) Mook, R., Jr.; Sher, P. M. *Org. Synth.* **1987**, *66*, 75.
(24) Lower selectivities have, however, been reported for the Et_3B-induced radical addition of triphenyltin hydride to alkynes.[8b]

Table III. Solvent Effect on the Orientation of Palladium- and Molybdenum-Catalyzed Hydrostannation of Oct-1-yn-3-ol *tert*-Butyldimethylsilyl Ether 7h

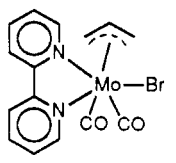
catalyst [M]	solvent	% convn[a] of **7h**	products (isomer ratio) **8h** (α isomer)/ **9h** (β isomer)
Pd	THF	100	28/72
	benzene	100	19/81
	CH_2Cl_2	100	13/87
Mo	THF	100	73/27
	benzene	53	57/43
	CH_2Cl_2	31	62/38

[a] 1.1 equiv of Bu_3SnH was used.

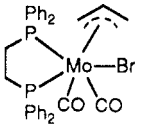
α-regioisomer (entries f–h, l). A similar (and apparently stronger) trend toward the formation of α-adducts is also observed with the rhodium catalyst.[17b]

For a given substrate, the regioselectivity is also somewhat dependent on the nature of the solvent (Table III). With both catalysts, use of the less polar solvents benzene or dichloromethane, rather than THF, results in better selectivity toward the formation of the β-isomer in the hydrostannation of the *tert*-butyldimethylsilyl ether of oct-1-yn-3-ol **7h**. Such variations in regioselectivity are probably under the control of coordinative interactions between the oxygen atom and the transition metal,[25] which must assume increasing importance as the polarity of the medium is lowered. As mentioned above, nonpolar solvents tend to be unsuitable for molybdenum catalysis, and low conversion of starting material is observed in benzene and in dichloromethane.

Attempts to modify the regiochemistry by changing the catalyst and, in particular, the steric bulk of the ligands, met with no success. Neither the bromodicarbonyl(2,2′-bipyridine)-π-allylmolybdenum complex (**12**)[20] nor the bromodicarbonyl(η^2-diphenylphosphinoethane)-π-allylmolybdenum complex (**13**)[20] catalyze the hydrostannation



12



13

$[(o\text{-tolyl})_3P]_2PdCl_2$

14

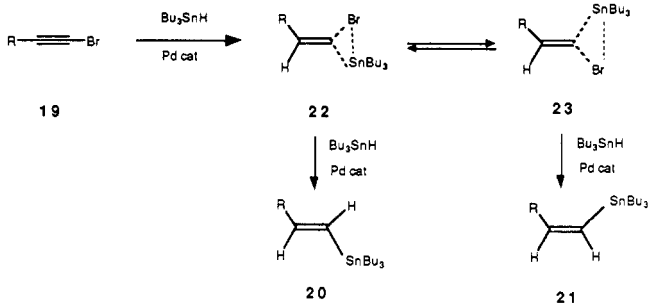
$[(MeO)_3P]_2PdCl_2$

15

process. The use of either the more bulky dichlorobis(tri-*o*-tolylphosphine)palladium complex (**14**) or of the less bulky dichlorobis(trimethylphosphite)palladium complex (**15**)[26] (in place of dichlorobis(triphenylphosphine)palladium, **1**) did not significantly affect the regiochemistry of hydrostannation of the *tert*-butyldimethylsilyl ether of oct-1-yn-3-ol. Furthermore, $PdCl_2[P(OMe)_3]_2$ is a poor catalyst and one which precipitates extensive decomposition of tributyltin hydride (eq 3); for the same reason, $PdCl_2(CH_3CN)_2$ is totally ineffective. Finally, lowering the temperature down to −10 °C did not materially affect the regiochemical outcome of the reactions catalyzed by complexes **1** or **3**.

Excluding certain specific substrates such as 2-butyne-1,4-diol **5a** (Table II), palladium is not a suitable catalyst for the hydrostannation of internal alkynes. By contrast,

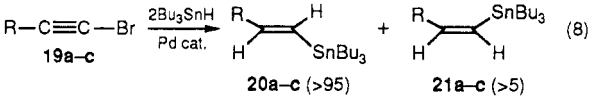
Scheme I



the molybdenum complex efficiently catalyzes the hydrostannation of disubstituted alkynes such as 4-octyne **5b** in virtually quantitative yield. Regardless of the choice of catalyst, hydrostannation of the more sterically congested internal alkynes, such as 6-undecyn-5-ol **5c**, is not complete, and a mixture of regioisomers is obtained.

B. Catalytic Hydrostannation of Heterosubstituted Acetylenic Compounds. The results for heterosubstituted alkynes **16a–e** are collected in Table IV. Ethoxyacetylene (with Pd catalyst) gives almost a 1/1 mixture of the two regioisomeric adducts. (Trimethylsilyl)acetylene does not react with tributyltin hydride in the presence of $PdCl_2(PPh_3)_2$. Similar deactivation of the acetylenic bond by the trimethylsilyl group toward both hydroalumination[27] and stannylcupration[9] has previously been observed by Zweifel. The molybdenum catalyst, on the other hand, permits the hydrostannation of (trimethylsilyl)acetylene with 100% conversion to give an 85:15 mixture of 1,1- and 1-(tributylstannyl)-2-(trimethylsilyl)-ethene, **17b** and **18b**. With 1-(trimethylsilyl)-1-hexyne, an opposite regioselectivity is observed, and the vicinally substituted (*E*)-1-(trimethylsilyl)-2-(tributylstannyl)-1-hexene (**18c**) is the major product. Bis(trimethylsilyl)-acetylene (**16d**) and 1-(tributylstannyl)-1-hexyne (**16e**) are strongly deactivated and are inert regardless of the catalyst used.

The reactivity of 1-halo-1-alkynes deserves special comment. In the presence of $PdCl_2(PPh_3)_2$, 1-bromo-1-alkynes **19a–c** react with 2 equiv of tributyltin hydride to give (*E*)-1-(tributylstannyl)-1-alkenes **20a–c** as the major products, together with trace amounts (<5%) of the *Z* isomers **21a–c** in 70–85% overall yields (eq 8). If only 1 equiv of tributyltin hydride is used, the yields of **20** and **21** drop to about 40%, and approximately half of the bromoacetylenic compound is recovered.



a, R = Bu; **b**, R = CH_2OTHP; **c**, R = $SiMe_3$

overall isolated yield of **20** + **21**: **a**, 85%; **b**, 70%; **c**, 62%

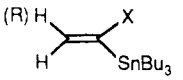
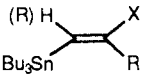
The intermediate formation of 1-alkynes, either by direct hydrostannolysis of the carbon–bromine bond or by an addition-elimination process, can be ruled out for these reactions. Indeed, we have found that the catalytic hydrostannation of 1-hexyne and of the THP derivative of propargyl alcohol gives a mixture of α- and β-adducts (Table I, entries c, k) while (trimethylsilyl)acetylene **16b** does not react with tributyltin hydride in the presence of palladium (Table IV). In order to account for the present results, it therefore seems necessary to assume that, in a first step, tributyltin hydride adds regioselectively to give

(25) Conversely, a coordination interaction between tin and oxygen is responsible for the hydrostannation of propargylic alcohols in the opposite direction (formation of "α-isomer") under radical conditions.[8a]

(26) The values of the ligand cone angle θ for P(*o*-tolyl)$_3$, PPh_3, and $P(OMe)_3$ are, respectively, 194°, 145°, and 107° (Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

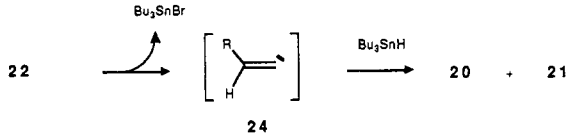
(27) Miller, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1983**, *105*, 1383.

Table IV. Palladium- or Molybdenum-Catalyzed Hydrostannation of Heterosubstituted Alkynes (except Haloalkynes: See the Text and eq 8 and 9)

starting alkyne (R)HC≡CX 16	catalyst [M]	 17	 18	isolated yield, %
HC≡COEt **16a**	Pd	**17a**/**18a** (42/58)		–[b]
HC≡CSiMe$_3$ **16b**	Pd Mo	no reaction **17b**/**18b** (85/15)		83[a]
n-BuC≡CSiMe$_3$ **16c**	Pd Mo	no reaction **17c**/**18c** (27/33)		80[a]
Me$_3$SiC≡CSiMe$_3$ **16d**	Pd, Mo	no reaction		
n-BuC≡CSnBu$_3$ **16e**	Pd, Mo	no reaction		

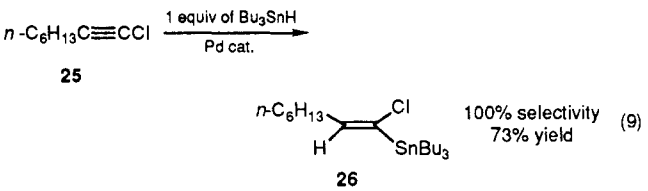
[a] Mixture of regioisomers. [b] The products were not isolated.

Scheme II

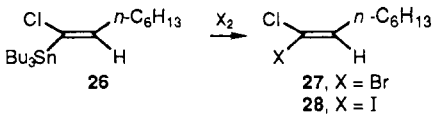


the 1-(tributylstannyl)-1-bromo-1-alkene **22** (Scheme I). This unstable alkylidene carbenoid species, with a greatly labilized carbon–bromine bond, would then undergo a fast[28] palladium-catalyzed cleavage by a second molecule of tributyltin hydride, to give the (*E*)-1-(tributylstannyl)-1-alkene, **20**. The formation of small amounts of the *Z* isomer **21** might possibly reflect some configurational lability of the carbenoid species (**22** ⇄ **23**). Another possibility (Scheme II) is that the carbenoid species **22** leads to the free alkylidene carbene **24**, which is then trapped by a second molecule of tributyltin hydride to give predominantly **20** and some **21**. Tributyltin hydride is, indeed, a very powerful trapping agent for carbenes.[29,30] Nevertheless, the alternative mechanism of Scheme II appears less plausible to us, as it is known that alkylidene carbenes with β-hydrogen substituents, such as **24**, are subject to spontaneous rearrangement to alkynes via hydrogen migration.

The mechanistic proposal of Schemes I–II is further supported by the results obtained with 1-chloro-1-octyne, **25**. Under palladium catalysis, **25** consumed only 1 equiv of tributyltin hydride, and (*E*)-1-chloro-1-(tributylstannyl)-1-octene (**26**) was obtained in 73% (isolated) yield, with total regio- and stereoselectivity (eq 9). Unlike its bromo analogues, **26** is sufficiently stable under the reaction conditions to resist further hydrostannolytic cleavage.



On reaction with either Br_2 or I_2 at low temperature, **26** gave (*E*)-1-chloro-1-bromo-1-hexene (**27**) and (*E*)-1-chloro-(*E*)-1-iodo-1-hexene (**28**) in 90% and 83% isolated yield (eq 10) with total conservation of stereochemistry. Thus, hydrostannation of chloroalkynes, followed by halodestannylation of the resulting chlorovinylstannane, should constitute a simple route to stereodefined 1-chloro-1-halo-1-alkenes, an interesting class of compounds which has traditionally been difficult to obtain.[31-33]



C. Catalytic Hydrostannation of Alkynes Bearing Conjugated Electronegative Substituents. Good regioselectivities were often achieved in the catalytic hydrostannation of alkynes bearing conjugated electronegative substituents (Tables V and VI).

α,β-Acetylenic Ketones or Esters. In the presence of palladium catalyst and 1 equiv of tributyltin hydride, conjugated alkynones and alkynoic esters **29** lead mainly to the corresponding (*E*)-α-(tributylstannyl)-α,β-unsaturated carbonyl compounds **30** (Table V). Total regioselectivity was found for all the alkynones studied, with the exception of 3-butyne-2-one **29a**, which bears no substituent at the terminal acetylenic carbon; this substrate produces a notable proportion (18%) of the β-tributylstannyl isomer **32a**. The reverse situation is observed with alkynoic esters. Methyl propynoate **29d** exclusively gives methyl α-(tributylstannyl)propenoate **30d**, but, rather surprisingly, concurrent formation of the β-tributylstannyl isomer (25%) is observed with methyl or allyl 2-heptynoates which bear an alkyl substituent at the C-3 acetylenic carbon. A greater tendency toward formation of the β-isomer is observed with the molybdenum catalyst (entries e and f). The overall strong preference for the formation of α-tributylstannyl isomers, at least in the palladium-catalyzed reactions, is consistent with a mechanism wherein tributyltin hydride formally acts as a hydride donor, as has already been inferred from the regiochemistry of catalytic hydrostannation of α,β-unsaturated ketones and nitriles.[34]

(28) Simple bromoalkenes are not as reactive. For instance, under similar conditions and due to competitive tributyltin hydride decomposition, 1-bromostyrene is reduced only to the extent of ca. 50% by addition of one equivalent of tributyltin hydride (observations from this laboratory).

(29) Stang, J. P. *Chem. Rev.* **1978**, *78*, 383. Stang, J. P. *Acc. Chem. Res.* **1982**, *15*, 348.

(30) Connor, J. A.; Day, J. P.; Turner, R. M. *J. Chem. Soc., Dalton Trans.* **1976**, 283. See also: Doyle, M. P.; Taunton, J.; Su-Min Oon, Liu, M. T. H.; Soundararajan, N.; Platz, M. S.; Jackson, J. E. *Tetrahedron Lett.* **1988**, *9*, 5863.

(31) Zweifel, G.; Lewis, W.; On, H. P. *J. Am. Chem. Soc.* **1979**, *101*, 5101.

(32) Zweifel, G.; Miller, J. A. *Org. React.* **1984**, *32*, 375.

(33) Fischer, R. P.; On, H. P.; Snow, J. T.; Zweifel, G. *Synthesis* **1982**, 127.

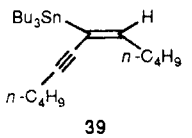
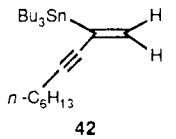
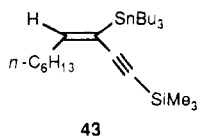
(34) Keinan, E.; Gleize, P. A. *Tetrahedron Lett.* **1982**, 477. Four, P.; Guibé, F. *Tetrahedron Lett.* **1982**, 1825. Keinan, E.; Greenspoon, N. *J. Org. Chem.* **1983**, *48*, 3545. Yang, T. X.; Four, P.; Guibé, F.; Balavoine, G. *Nouv. J. Chim.* **1984**, *8*, 611.

Table V. Palladium- and Molybdenum-Catalyzed Hydrostannation of Conjugated Alkynes (Conjugated Diynes Are Reported Separately in Table VI)

			product (% ratio)			
			RHC=C(Σ)SnBu$_3$		Bu$_3$Sn(R)C=CHΣ	
entry	starting alkyne RC≡CΣ **29**	catalyst [M]	*E* **30**	*Z* **31**	*E* **32**	isolated yield, %
a	HC≡CCOMe **29a**	Pd	82		18	65
b	*n*-C$_6$H$_{13}$C≡CCOMe **29b**	Pd	100	0	0	0[a,b]
c	*n*-C$_4$H$_9$C≡CCOPh	Pd	58	42	0	0[a]
	29c	Mo	66	34	0	0[a]
d	HC≡CCO$_2$Me **29d**	Pd	100		0	94
e	*n*-C$_4$H$_9$C≡CCO$_2$Et	Pd	75	0	25	83[c]
	29e	Mo	24	0	76	78[c]
f	*n*-C$_4$H$_9$C≡CCO$_2$CH$_2$CH=CH$_2$	Pd	74	0	26	76[c]
	29f	Mo	32	0	68	–[e]
g	Me$_3$SiC≡CCO$_2$Et **29g**	Pd	100	0	0	71
h	Me$_3$SiC≡CCOMe **29h**	Pd, Mo	–	–	–	–[d]
i	MeC≡CPh	Pd	100	0	0	79
	29i	Mo	48	0	52	–[e]
j	HC≡CPh	Pd	38	0	62	–[e]
	29j	Mo	47	0	53	56

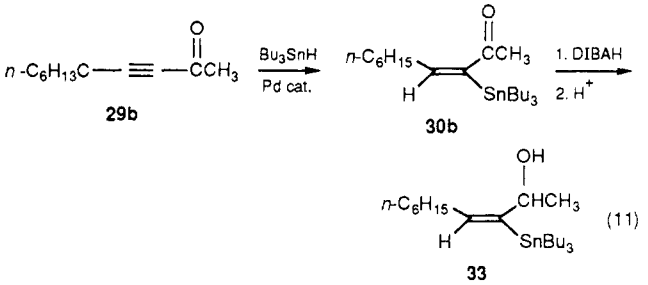
[a] Total protodestannylation occurred during attempted purification by chromatography (see the text). [b] In situ reduction of **30b** by DIBAL gave the corresponding alcohol **33** in 61% yield (see eq 11 and the text). [c] Isolated as a mixture of regioisomers. [d] No hydrostannation products could be detected (see the text). [e] The products were not isolated.

Table VI. Palladium-Catalyzed Hydrostannation of Conjugated Diynes

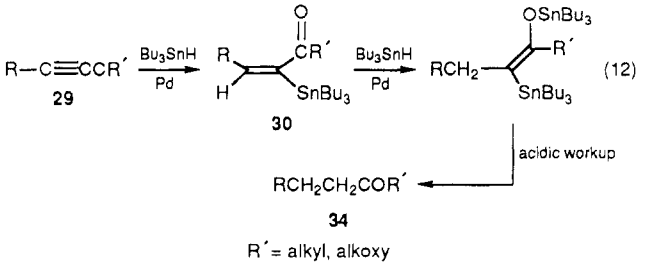
starting material	product	isolated yield, %
n-C$_4$H$_9$C≡CC≡C-*n*-C$_4$H$_9$ **38**	 **39**	78
n-C$_6$H$_{13}$C≡CC≡CH **40**	 **42**	54
n-C$_6$H$_{13}$C≡CC≡CSiMe$_3$ **41**	 **43**	86

The stereochemistry of hydrostannation of carbonyl conjugated alkynes is cis, leading to products of *E* configuration. The mixture of *E* and *Z* isomers which is obtained as a result of the hydrostannation of 1-phenyl-2-heptyn-1-one (**29c**) probably arises from configurational lability of the principally formed *E* isomer **30c**. α-Tributylstannyl conjugated enones are very sensitive to acidic conditions, and attempted purification by column chromatography on silica gel resulted, except for **29a**, in complete protodestannylation. α-(Tributylstannyl)-α,β-unsaturated esters however, are stable enough to undergo purification by this method.

Due to the configurational and chemical fragility of α-tributylstannyl conjugated enones, it is best to use them without delay following the hydrostannation step. Thus 3-decyn-2-one **29b** was allowed to react first with tributyltin hydride in the presence of palladium, and then with diisobutylaluminum hydride to give, after chromatography, pure (*E*)-3-(tributylstannyl)-3-decen-2-ol (**33**) in 61% overall yield from **29b** (eq 11).

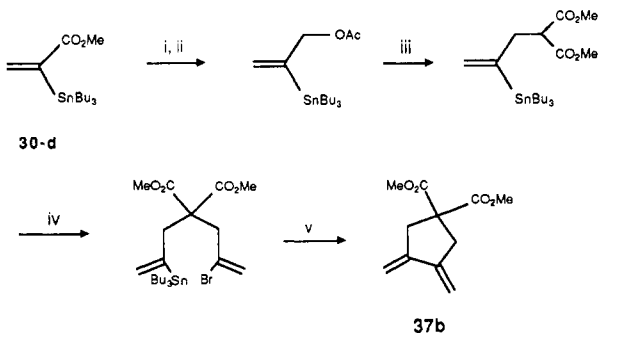


If an excess of tributyltin hydride is used in the catalytic hydrostannation of conjugated alkynones or alkynoates, the first-formed α-(tributylstannyl)enones or enoates tend to undergo further hydrostannation, probably in a 1,4-manner, to give, after protonolysis, the saturated carbonyl compound **34** (eq 12). Such catalytic 1–4 hydrostannations have been recently observed with ordinary conjugated enones.[34] The second hydrostannation step in eq 12 is difficult, however, and extensive decomposition of tributyltin hydride is simultaneously observed.



In the reaction of allyl 3-heptynoate with 1 equiv of tributyltin hydride, formation of tributyltin ester could not be observed. This result indicates that the palladium-catalyzed hydrostannation reaction of the carbonyl-con-

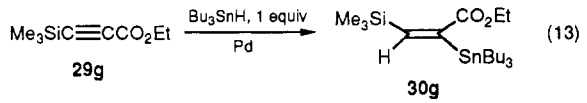
Scheme III[a]



[a] (i) DIBAH, Et_2O, −78 °C; (ii) Ac_2O, DMAP, Py (i × ii = 44%); (iii) dimethylmalonate sodium salt, THF, $Pd(PPh_3)_4$ 5%, PPh_3 10%, room temperature, 6 h (87%); (iv) HNa, then $BrCH_2C(Br)=CH_2$, THF, room temperature, 18 h (74%); (v)[2a] $PdCl_2(CH_3CN)_2$ 5%, DMF, room temperature, 20 h (66%).

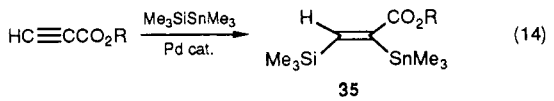
jugated triple bond is a much more rapid process than the palladium-catalyzed hydrostannolytic cleavage of the allyl group.[35]

Ethyl 3-(trimethylsilyl)propynoate (**29g**) reacts with 1 equiv of tributyltin hydride to give, regio- and stereoselectively, ethyl (*E*)-2-(tributylstannyl)-3-(trimethylsilyl)-propenoate (**30g**) in 70% yield (Table V and eq 13). This



(13)

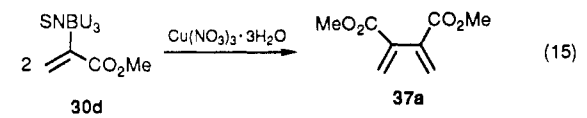
reaction complements the palladium-catalyzed addition of (trimethylsilyl)trimethylstannane to propynoic esters, which yields the product **35** with the same regiochemistry but the opposite *Z* stereochemistry[13] (eq 14).



(14)

We were not able to obtain a hydrostannation product from β-(trimethylsilyl)alkynones (Table V, entry h). Instead, a complex mixture of unidentified volatile products was obtained.

α-Tributylstannyl α,β-unsaturated ketones or esters such as **30a,b,d,g** could be useful synthons and are not readily obtained by other means.[36,37] As an illustrative example, we have synthesized **37a**[38] from methyl 2-(tributylstannyl)propenoate (**30d**) in one step and in 58% yield by copper(II) mediated coupling[6] of **30d** (eq 15). In another



(15)

example, the bis(*exo*-methylene)cyclopentane derivative **37b**[39] was synthesized according to Scheme III.

Conjugated Phenyl Alkynes (Table V). The palladium-catalyzed hydrostannation of 1-phenyl 1-propyne selectively gives (*E*)-1-phenyl-1-(tributylstannyl)propene, but the regioselectivity is lost in the case of phenylethyne (entries i, j). A mixture of α- and β-regioisomers is obtained with both alkynes when the molybdenum catalyst is used.

Conjugated Diynes (Table VI). The reaction was first carried out on the symmetrically substituted 3,5-dodecadiyne **38** with palladium as the catalyst. Upon reaction with 1.1 equiv of tributyltin hydride, **38** chemo-, regio-, and stereoselectively yields the monohydrostannation *E* adduct **39**, in which the tributylstannyl group is located on the carbon atom adjacent to the unreacted triple bond. Here again the sense of addition is consitent with a mechanism in which tributyltin hydride acts as a hydride donor in the presence of palladium catalyst. Upon addition of more tributyltin hydride, **39** undergoes further hydrostannation only with extreme difficulty, and considerable tin hydride decomposition is observed.

We next examined the hydrostannation of the terminal 1,3-diyne **40** and of its 1-(trimethylsilyl) analogue **41**, in hopes of achieving chemoselective reactions. Indeed, **40** reacts specifically at the terminal triple bond to chemo- and regioselectively give the (*E*)-2-(tributylstannyl) enyne derivative **42**. From the earlier observation (Table IV, entry b) that (trimethylsilyl)acetylenes do not react with tributyltin hydride in the presence of palladium, as well as from Zweifel's results on the hydroalumination[27] and on the cuprostannylation[9] of 1-(trimethylsilyl)-1,3-diynes, it might be expected that, contrary to **40**, **41** would react preferentially at the internal triple bond. Indeed, **41**, was found to give, with excellent chemo-, regio-, and stereoselectivity, (*E*)-1-(trimethylsilyl)-3-(tributylstannyl)-3-decen-1-yne, **43**. Compounds such as **42** and **43**, with well-defined regio- and stereochemical structures, are likely to be useful derivatives in synthetic chemistry. The utilization of related synthons has recently been described by Zwiefel.[9]

Conclusion

In conclusion, the palladium and molybdenum complexes **1** and **3** are very efficient catalysts for the tributyltin hydride hydrostannation of alkynes. The catalytic reactions are very easy to perform and occur under very mild conditions. They are totally stereospecific (cis hydrostannation), and good or complete regioselectivity is observed in many instances. Total regioselectivity is realized for substrates such as terminal alkynes bearing a sufficiently bulky substituent, some heterosubstituted alkynes ((trimethylsilyl)acetylene, chloroalkynes) as well as alkynes conjugated with electron-withdrawing groups, e.g. conjugated alkynones, alkynoic esters, and 1,3-diynes. When the direct hydrostannation of monosubstituted alkynes results in poor regioselectivity, the corresponding (*E*)-1-(tributylstannyl)-1-alkene may, nevertheless, be obtained selectively (albeit in a roundabout way) through bromination of the alkyne followed by palladium-catalyzed reduction of the bromoalkyne with 2 equiv of tributyltin hydride. In summary, the catalytic reactions presented herein constitute a novel route to interesting vinylstannane synthons. They should complement well the usual radical hydrostannation reactions, as well as the methods based on the utilization of trialkylstannyl metal species.

Experimental Section

General Methods. IR spectra were recorded on a Perkin-Elmer Model 880 instrument. ^1H NMR spectra ($CDCl_3$) were obtained at 250 MHz with a Bruker AM 250 or at 200 MHz with a Bruker AC 200 instrument. Chemical shifts are reported in ppm units, by reference to Me_4Si. When necessary, unambiguous assignments were made by decoupling experiments. ^{13}C NMR spectra ($CDCl_3$) were recorded with a Bruker AC 200 instrument at 50.288 MHz. Chromatographic separations of tin compounds

(35) Saint M'Leux, Y.; Guibé, F. *Tetrahedron Lett.* **1981**, 3591. Keinan, E.; Greenspoon, N. *Tetrahedron Lett.* **1982**, 241.
(36) See, for instance: Zapata, A.; Fortoul, C.; Carola Acuña, A. *Synth. Commun.* **1985**, *15*, 179.
(37) See, for instance, ref 1b, 2d, 11 and the following: Piers, E.; Karumaratne, V. *J. Org. Chem.* **1983**, *48*, 1774.
(38) Tarnchompoo, B.; Thebtaranonth, C.; Thebtaranonth, Y. *Tetrahedron Lett.* **1987**, *28*, 6671, 6675.
(39) Grigg, R.; Stevenson, P.; Worrakun, T. *Tetrahedron* **1988**, *44*, 2049. Trost, B. M.; Lee, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 7255.

were performed by using 70–230 mesh silica gel. Precoated silica gel plates Merck F-254 were used for thin-layer analytical chromatography. GLC analyses were performed on a Fractovap 4130 Model equiped with a SE 54 coated 15-m glass capillary column. GLC/MS analysis were carried out on a Nermag R-10-10 apparatus connected to a CPSILS quartz capillary column. The purity of all title compounds was judged to be ≥90% by GC and/or ^{13}C and ^1H NMR spectral determinations. Spectra appear in the supplementary material.

THF and diethyl ether were freshly distilled over sodium benzophenone ketyl and dichloromethane; benzene and pyridine were distilled over finely powdered calcium hydride. All manipulations involving transition metal complexes were carried out under argon atmosphere using vacuum line, syringe/septum, and Schlenk tube techniques.

Materials. The preparation and storage of tributyltin hydride has already been described.[19b] $PdCl_2(PPh_3)_2$ was obtained as previously indicated.[19b] Due to the very low solubility of tri-*o*-tolylphosphine in ethanol, $PdCl_2[P(o\text{-tolyl})_3]_2$ was prepared in a slightly different way: After addition of the methanolic solution of Na_2PdCl_4 to a suspension of 2.05 equiv of tri-*o*-tolylphosphine in absolute ethanol, the reaction mixture was refluxed for 30 min and cooled to room temperature. The solid was purified as described for $PdCl_2(PPh_3)_2$. Yield: 89%. IR (Nujol mull, ICs plates): 351 cm^{-1} (Pd–Cl) (lit.[40] 351 cm^{-1}). The following complexes were prepared and characterized by IR or NMR data as reported in the literature: $PdCl_2(CH_3CN)_2$,[41] $PdCl_2[P(OMe)_3]_2$,[42] $(CH_3CN)_2Mo(CO)_2(\pi\text{-allyl})Br$,[20] (bipy)$Mo(CO)_2(\pi$-allyl)Br,[20] (dppe) $Mo(CO)_2(\pi$-Allyl)Br.[20] The following alkynes were commercially availble and distilled whenever necessary: propargyldimethylamine, 3-butyn-2-ol, 2-methyl-3-butyn-2-ol, 1-octyn-3-ol, 1-phenyl-2-propyn-1-ol, 1-hexyne, 1-octyne, 2-butyne-1,4-diol, 4-octyne, ethoxyacetylene, (trimethylsilyl)acetylene, bis(trimethylsilyl)acetylene, butyn-2-one, methyl propynate, phenylacetylene, 1-phenyl-1-propyne. The THP derivative (bp 76–77 °C/18 mmHg) and the *tert*-butyldimethylsilyl derivative (purified by column chromatography on silica gel, cyclohexane/AcOEt, 11/1) of propargyl alcohol were prepared according to standard procedure.[43] 3-*n*-Pentyl-1-octyne was prepared by the alkylation of the dilithium salt of 1-octyn[44] with *n*-pentyl bromide, bp 85 °C/6.5 mmHg. ^1H NMR: 2.31 (m, 1 H), 2.05 (d, J = 2 Hz, 1 H), 1.56–1.20 (m, 16 H), 0.89 (t, J = 6.5 Hz, 6 H). 6-Undecyn-5-ol was prepared according to a published procedure.[45] The ethyl and allyl esters of 2-heptynoic acid were prepared by reacting the corresponding chloroformates with the bromomagnesium salt of 1-hexyne:[46] bp 60 °C/1 mmHg and 62 °C/0.7 mmHg, respectively. ^1H NMR for allyl 2-heptynoate: 6.03–5.82 (m, 1 H, internal vinylic H), 5.38 (dd, $^3J_{trans}$ = 17 Hz, ^2J = 0.5–1 Hz, 1 H, *Z* terminal vinylic H), 5.28 (dd, $^3J_{cis}$ = 10 Hz and 0.5–1 Hz, 1 H, *E* terminal vinylic H), 4.67 (d, J = 6 Hz, 2H, allylic H), 2.35 (t, J = 7.5 Hz, 2 H), 1.65–1.30 (m, 4 H), 0.94 (t, J = 7.5 Hz, 3 H). 1-(Trimethylsilyl)-1-hexyne (bp 74 °C/40 mmHg) and 1-(tributylstannyl)-1-hexyne (bp 100 °C/0.2 mmHg) were obtained by reacting the lithium salt of 1-hexyne with trimethylchlorosilane[47] and tributylstannyl chloride,[48] respectively. 3-Decyn-2-one[49] (bp 55 °C/0.3 mmHg), 1-phenyl-2-heptyn-1-one,[49] 5,7-dodecadiyne,[50] and 1-(trimethylsilyl)-1,3-decadiyne[51] were prepared according to literature procedures. 1,3-Decadiyne was obtained by Kende's method,[52] starting from (*Z*)-1,2-dichloroethene and 1-octyne; it was purified by column chromatography (silica gel, hexane). Ethyl 3-(trimethylsilyl)propynoate,[46] 4-(trimethylsilyl)butyn-2-one,[46] (bromoethynyl)trimethylsilane,[51] and 1-chloro-1-octyne[53] were prepared according to literature procedures. 1-Bromo-1-hexyne (bp 60 °C/50 mmHg) and the THP derivative of 1-bromopropynol (bp 79–81 °C/0.2 mmHg) were obtained by reacting the lithium salts of 1-hexyne and of the THF derivative of propynol with bromine.[54] ^1H NMR data for the THP derivative of 1-bromopropynol: 4.81 (m, 1 H, H-2 of THP), 4.28 (AB system, J_{AB} = 16 Hz, 2 H, propargylic H), 3.83 (m) and 3.54 (m, 2 H, H-6_{eq} and H-6_{ax} of THP), 1.92–1.43 (m, 6 H).

General Procedure for Catalytic Hydrostannation of Alkynes. This procedure is, in almost every aspect, similar to the one used for catalytic hydrostannolysis of acyl chlorides to aldehydes.[55] Reactions were generally performed on a 10^{-2} to 10^{-3} molar scale. They were carried out at room temperature under an argon atmosphere. After completion of the reaction, the vinylstannanes were purified by column chromatography; for the less polar compounds, complete separation from small amounts of hexabutyldistannane was sometimes difficult to achieve.

In a typical experiment, to a THF solution (3 mL) of 3-*n*-pentyl-1-octyne (180 mg, 1 mmol) containing $PdCl_2(PPh_3)_2$ (14 mg, 0.02 equiv) was added tributyltin hydride dropwise with a syringe over a period of ca. 1–2 min. After ca. 1.1 equiv of Bu_3SnH had been added, the originally light yellow solution abruptly turned orange-brown. An additional 0.1 equiv of tributyltin hydride was added, and stirring was continued for about 10 min. THF was then evaporated on a Rotovap. The oily residue which was now contaminated with black palladium impurities was purified by column chromatography (silica gel, cyclohexane). Hexabutyldistannane was eluted first, followed immediately by (*E*)-1-(tributylstannyl)-3-*n*-pentyl-1-pentene. Yield: 423 mg (90%). The molybdenum-catalyzed reaction (0.4 equiv of catalyst) was conducted in a similar way. Yield: 422 mg (89%). In this case, the end of the reaction is signaled by a sudden color change of the solution, from dark purple to black.

Physical and Spectroscopic Characteristics of Alkenylstannanes. ^1H NMR of the tributylstannyl groups are found at 1.6–1.2 ppm (m, 18 H) and at 0.9 ppm (t, J = 7 Hz, 9 H) in all alkenylstannanes. These values are not included in the listing of ^1H NMR resonances. Both $J(^{117}SnH)$ and $J(^{119}SnH)$ values are reported when the ^{119}Sn and ^{117}Sn satellite peaks are clearly distinct. Otherwise the indicated J_{SnH} values must be considered as an approximate mean value of $J(^{117}SnH)$ and $J(^{119}SnH)$. The MS m/e peaks marked with an asterisk correspond to tin-containing fragments and refers to the main isotopic peak (^{120}Sn). Other isotopic satellites are omitted. 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.

8a. ^1H NMR: 5.88 (dt, $J_d = J_t$ = 2 Hz, 1 H, $^3J_{SnH}$ = 128 Hz, *E* vinylic H), 5.24 (dt, $J_d = J_t$ = 2 Hz, 1 H, $^3J_{SnH}$ = 60 Hz, *Z* vinylic H), 4.29 (m, 2 H, $^3J_{SnH}$ = 28 Hz, allylic H). **9a.** ^1H NMR: 6.35–6.03 (m, 2 H, vinylic H), 4.18 (m, 2 H, allylic H). (**8a + 9a**) Anal. Calcd for $C_{15}H_{32}OSn$: C, 51.91; H, 9.29. Found: C, 52.07; H, 9.50.

8b. ^1H NMR: 7.22 (m, 2 H) and 6.88 (m, 3 H), 5.96 (dt, $J_d = J_t$ = 2 Hz, 1 H, $^3J_{SnH}$ = 128 Hz), 5.35 (dt, $J_d = J_t$ = 2 Hz, 1 H, $^3J_{SnH}$ = 60 Hz)e, 4.64 (dd, J = 2 Hz, 2 H, $^3J_{SnH}$ = 32 Hz). GC/MS: 367* (61, $M^+ - C_4H_9$), 327* (100, $M^+ - PhO$), 213* (97), 179* (14), 177* (24), 121* (20), 57 (12), 41 (17). **9b.** ^1H NMR: 7.22 (m, 2 H) and 6.88 (m, 3 H), 6.35 (dt) and 6.18 (dt, ABX_2 system, J_{AB} = 20 Hz, J_{AX} = 1 Hz, J_{BX} = 5 Hz, 2 H), 4.53 (dd, J = 1 and 5 Hz, 2 H). GC/MS: 367* (100, $M^+ - C_4H_9$), 311* (34), 255* (18), 253* (19), 213* (39), 177* (13.5), 117 (27), 91 (11).

8c. ^1H NMR: 5.88 (dt, $J_d = J_t$ = 2 Hz, 1 H, $^3J_{SnH}$ = 130 Hz), 5.25 (dt, $J_d = J_t$ = 2 Hz, 1 H, $^3J_{SnH}$ = 63 Hz), 4.68 (dd, J = 3 Hz, 1 H, H-2(THP)), 4.48–4.34 (m) and 4.10–3.97 (m) (2 H, allylic H), 3.95–3.80 (m) and 3.58–3.44 (m, 2 H, H-6_{ax} and H-6_{eq}(THP)).

(40) Bennet, A. M.; Bramley, R.; Longstaff, P. A. *J. Chem. Soc., Chem. Commun.* **1966**, 806.
(41) Hartley, F. R.; Murray, S. G.; Mc Auliffe, C. A. *Inorg. Chem.* **1979**, *18*, 1394.
(42) Jenkins, J. M.; Verkade, J. G. *Inorg. Chem.* **1967**, *6*, 2250. Goodfellow, R. J.; Taylor, R. F. *J. Chem. Soc., Dalton Trans.* **1974**, 1676.
(43) Greene, T. W. *Protective Groups in Organic Syntheis*; John Wiley: New York, 1981.
(44) Sagar, A. J. G.; Scheinmann, F. *Synthesis* **1976**, 321.
(45) Colas, Y.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1984**, *25*, 845; *Bull. Soc. Chim. Fr.* **1987**, 165.
(46) Kraihanzel, C. S.; Losee, M. L. *J. Org. Chem.* **1968**, *33*, 1983.
(47) Zweifel, G.; Backlund, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 3184.
(48) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138.
(49) Brown, H. C.; Racherla, V. S.; Singh, S. M. *Tetrahedron Lett.* **1984**, *25*, 2411.
(50) Rossi, R.; Carpita, A.; Bigelli, C. *Tetrahedron Lett.* **1985**, *26*, 523.
(51) Miller, J. A.; Zweifel, G. *Synthesis* **1983**, 128.
(52) Kende, A. S.; Smith, C. A. *J. Org. Chem.* **1988**, *53*, 2655.
(53) Murray, R. E. *Synth. Commun.* **1980**, *10*, 345.
(54) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: New York, 1971; p 98.
(55) Four, P.; Guibe, F. *J. Org. Chem.* **1981**, *46*, 4439.

GC/MS: 375* (100, $M^+ - C_4H_9$), 335* (37), 291* (29), 251* (84.5), 179* (37), 177* (54), 137* (25), 121* (27), 85 (39), 67 (16), 57 (25), 41 (43). **9c.** ^1H NMR: 6.23 (d) and 6.07 (dt) (ABX_2 system, J_{AB} = 19 Hz, J_{AX} = 0, J_{BX} = 5 Hz, 2 H), 4.65 (dd, J = 3 Hz, 1 H, H-2(THP)), 4.34–4.24 (m) and 4.10–3.97 (m, 2 H, allylic H), 3.95–3.80 (m) and 3.58–3.44 (m, 2 H, H-6_{ax} and H6_{eq}(THP)). GC/MS: 375* (90, $M^+ - C_4H_9$), 291* (20), 177*(30), 137* (11), 121* (13), 85 (100), 67 (17), 57 (17), 55 (16), 41 (28). (**8c + 9c**) Anal. Calcd for $C_{20}H_{40}O_2Sn$: C, 55.71; H, 9.35. Found: C, 55.43; H, 9.26.

8d. ^1H NMR 5.77 (dt, J_d = 3 Hz, J_t = 1.5 Hz, 1 H, $^3J_{SnH}$ = 140 Hz), 5.19 (dt, J_d = 3 Hz, J_t = 1.5 Hz, 1 H, $^3J_{SnH}$ = 64 Hz), 2.95 (m, 2 H, $^3J_{SnH}$ = 46 Hz), 2.12 (s, 6 H). GC/MS: 3.18* (100) ($M^+ - C_4H_9$), 233* (12.5), 179* (27), 177* (28), 121 (20), 84 (69), 58 (65), 42 (16). **9d.** ^1H NMR: 6.10 (d) and 6.00 (dt), (ABX_2 system, J_{AB} = 19 Hz, J_{AX} = 0 Hz, J_{BX} = 5 Hz, 2 H), 2.95 (d, J = 5 Hz, 2 H), 2.23 (s, 6 H). GC/MS: 318* (26), 262* (7), 177* (5), 121* (5), 84 (100), 58 (72). (**8d + 9d**) Anal. Calcd for $C_{17}H_{37}NSn$: C, 54.57; H. 9.97. Found: C, 54.68; H, 9.82.

8e. ^1H NMR: 5.74 (m, 1 H, $^3J_{SnH}$ = 134 Hz), 5.11 (m, 1 H, $^3J_{SnH}$ = 63 Hz), 4.35 (q, J = 6 Hz, 1 H). **9e.** ^1H NMR: 6.08 (d) and 5.99 (dd) (ABX system, J_{AB} = 20 Hz, J_{AX} = 0 Hz, J_{BX} = 4 Hz, 2 H), 4.19 (dq, J_d = 4 Hz, J_q = 6 Hz, 1 H).

8f. ^1H NMR: 5.63 (s, 1 H, $^3J_{SnH}$ = 142 Hz), 5.05 (s, 1 H, $^3J_{SnH}$ = 70 Hz). **9f.** ^1H NMR: 6.03 (broad s, 2 H, $^2J_{SnH} \simeq {}^3J_{SnH} \simeq$ 70 Hz). Anal. Calcd for $C_{17}H_{36}OSn$: C, 54.43; H, 9.69. Found: C, 54.37; H, 9.38.

8g. ^1H NMR: 5.77 (m, 1 H, $^3J_{SnH}$ = 134 Hz), 5.20 (m, 1 H, $^3J_{SnH}$ = 61 Hz), 4.16 (broad t, J = 6 Hz, 1 H). **9g.** ^1H NMR: 6.13 (d) and 5.99 (dd) (ABX system, J_{AB} = 19 Hz, J_{AX} = 0 Hz, J_{BX} = 5 Hz, 2 H), 4.04 (dt, $J_d = J_t$ = 5 Hz, 1 H). (**8g + 9g**) Anal. Calcd for $C_{15}H_{32}OSn$: C, 57.57; H, 10.15. Found: C, 57.69; H, 10.51.

8h. ^1H NMR: 5.71 (m, 1 H, $^3J_{SnH}$ = 136 Hz), 5.13 (m, 1 H, $^3J_{SnH}$ = 65 Hz), 4.11 (t, J = 6 Hz, 1 H). GC/MS: 475* (54, $M^+ - C_4H_9$), 365* (100), 309* (14), 281* (32), 251* (15), 225* (31), 211* (14), 209* (26), 195* (46), 179* (17), 177* (20), 121* (11), 75 (19), 73 (29), 57 (26.5), 41 (16). **9h.** ^1H NMR: 6.03 (d) and 5.91 (dd) (ABX system, J_{AB} = 19 Hz, J_{AX} = 0 Hz, J_{BX} = 5 Hz, 2 H), 4.03 (dt, J = 5 Hz, 1 H). GC/MS: 475* (96, $M^+ - C_4H_9$), 249* (22), 241 (14), 225 (17), 209* (18), 195* (30), 193* (61), 179* (20), 177* (29), 75 (45), 73 (100), 57 (26), 41 (12). (**8h + 9h**) Anal. Calcd for $C_{26}H_{56}OSiSn$: C, 58.76; H, 10.62. Found: C, 59.21; H, 10.02.

8i. ^1H NMR: 7.45–7.10 (m, 5 H), 5.89 (m,1 H), 5.30 (m, 1 H), 5.23 (s, 1 H). **9i**: 7.45–7.10 (m, 5 H), 6.27 (d) and 6.13 (dd) (ABX system, J_{AB} = 19 Hz, J_{AX} = 0 Hz, J_{BX} = 5 Hz, 2 H).

8j. ^1H NMR: 5.65 (m, 1 H, $^3J_{SnH}$ = 142 Hz), 5.08 (m, 1 H, $^3J_{SnH}$ = 65 Hz), 2.24 (t, J = 7 Hz, 2 H). **9i.** ^1H NMR: 5.95 (dt) and 5.84 (d) (ABX_2 system, J_{AB} = 19 Hz, J_{AX} = 5 Hz, J_{BX} = 0 Hz, 2 H), 2.13 (dt, J = 5 Hz and 7 Hz, 2 H).

8k. ^1H NMR: 5.65 (dt, J_d = 3 Hz, J_t = 1.5 Hz, 1 H, $^3J_{SnH}$ = 140 Hz), 5.09 (d, J = 3 and 1 Hz, $^3J_{SnH}$ = 64 Hz), 2.24 (broad t, J = 7 Hz, $^3J_{SnH}$ = 46 Hz). GC/MS: 319* (100, $M^+ - C_4H_9$), 261* (64), 205 (78), 179* (17), 177* (22), 121* (52), 41 (19). **9k.** ^1H NMR: 5.96 (dt) and 5.84 (d) (ABX_2 system, J_{AB} = 19 Hz, J_{AX} = 5 Hz, J_{BX} = 0 Hz, 2 H), 2.13 (dt, J = 5 and 7 Hz, 2 H). GC/MS: 317* (100, $M^+ - C_4H_9$), 261* (52), 205* (62), 179* (11), 177* (14), 121* (33), 81* (21), 41* (13).

8l. ^1H NMR: 5.60 (d, J = 2 Hz, 1 H, $^3J_{SnH}$ = 140 Hze, 5.10 (d, J = 2 Hz, 1 H, $^3J_{SnH}$ = 66 Hz), 2.10 (m, 1 H). GC/MS: 415* (100, $M^+ - C_4H_9$), 359* (23), 303* (13), 179* (28), 177* (30), 121* (24), 69 (13), 55 (19), 41 (17). **9l.** ^1H NMR: 5.77 (d, 1 H, $^2J_{SnH}$ = 80 Hz) and 5.60 (dd, 1 H, $^3J_{SnH}$ = 68 Hz); (ABX system, J_{AB} = 19 Hz, J_{BX} = 0 Hz, J_{BX} = 8 Hz), 1.95 (m, 1 H). GC/MS: 415* (100, $M^+ - C_4H_9$), 359* (23), 303* (25), 179* (16), 177* (20), 121* (25), 69 (11), 55 (14), 43 (15). Anal. Calcd for $C_{25}H_{52}Sn$: C, 63.70; H, 11.12. Found: C, 63.67; H, 11.26.

6a. ^1H NMR: 5.80 (tt, J = 6 and 2 Hz, 1 H, $^3J_{snH}$ = 68 Hz), 4.40 (s, 2 H, $^3J_{SnH}$ = 36 Hz), 4.21 (d, J = 6 Hz, 2 H), 1.70 (broad s, 2 H).

6b. ^1H NMR: 5.50 (tt, J = 7 and 1 Hz, 1 H, $^3J_{SnH}$ = 74 Hz), 2.22 (t, J = 7.5 Hz, 2 H, $^3J_{SnH}$ = 60 Hz), 2.10 (dt, J = 7 and 7.5 Hz, 2 H). GC/MS: 345* (100, $M^+ - C_4H_9$), 289* (41), 233* (53), 179* (28), 177* (32), 175 (27). Anal. Calcd for $C_{20}H_{42}Sn$: C, 59.87; H, 10.55. Found: C, 60.98; H, 10.58.

6ca. ^1H NMR: 5.48 (t, J = 7 Hz, 1 H, $^3J_{snH}$ = 72 Hz), 4.65 (m, 1 H, $^3J_{SnH}$ = 70 Hz), 2.20–1.90 (m, 2 H). GC/MS: 403* (14, $M^+ - C_4H_9$), 385* (70), 271* (5), 251* (100), 177* (16), 137* (24), 81 (13), 67 (13), 57 (72), 41 (13). **6cb.** ^1H NMR: 5.51 (d, J = 8 Hz, 1 H, $^3J_{SnH}$ = 71 Hz), 4.50 (m, 1 H), 2.30 (t, J = 7 Hz, 2 H). GC/MS: 403* (100, $M^+ - C_4H_9$), 385* (19), 347* (17), 291* (11), 251* (19), 235* (77), 177* (23), 137* (16), 121* (14), 95 (15), 81 (12), 67 (15), 55 (19), 41 (15).

17a. ^1H NMR: 4.67 (d, J = 3 Hz, 1 H, $^3J_{SnH}$ = 100.5 Hz), 4.05 (d, J = 3 Hz, 1 H, $^3J_{SnH}$ = 30 Hz), 3.70 (q, J = 7.5 Hz, 2 H). **18a.** ^1H NMR: 6.23 (d, J = 16 Hz, 1 H, $^3J_{SnH}$ = 35 Hz), 4.67 (d, J = 16 Hz, 1 H, $^2J_{SnH}$ = 40.5 Hz), 3.80 (q, J = 7.5 Hz, 2 H).

17b. ^1H NMR: 6.48 (d, J = 4.5 Hz, 1 H, $^3J(^{117}SnH)$ = 172 Hz, $^3J(^{119}SnH)$ = 178 Hz), 6.21 (d, J = 4.5 Hz, 1 H, $^3J(^{117}SnH)$ = 104 Hz, $^3J(^{119}SnH)$ = 108 Hz), 0.07 (s, 9 H). GC/MS: 333* (100, $M^+ - C_4H_9$), 227* (47), 221* (58), 193* (18), 179* (30), 135* (18), 121* (25), 73 (68), 59 (24),41 (11). **18b.**[56] ^1H NMR: 6.97 (d, J = 22 Hz, 1 H), 6.61 (d, J = 22 Hz, 1 H), 0.07 (s, 9 H). GC/MS: 333* (92, $M^+ - C_4H_9$), 277* (49), 221* (43), 179* (64), 121* (27), 73 (100), 59 (10), 45 (10). (**17c + 18c**) Anal. Calcd for $C_{17}H_{38}SiSn$: C, 52.46; H, 9.84. Found: C, 52.89; H, 9.92.

17c. ^1H NMR: 6.35 (t, J = 7.5 Hz, 1 H, $^3J_{SnH}$ = 112 Hz), 2.10 (dt, J = 7.5 Hz, 2 H). GC/MS: 389* (100, $M^+ - C_4H_9$), 333* (14), 235* (30), 207* (12), 193* (33), 135* (17), 121* (22), 73 (98), 41 (15). **18c.** ^1H NMR: 5.64 (s, 1 H, $^3J_{SnH}$ = 100 Hz), 2.23 (t, J = 7.5 Hz, 2 H). GC/MS: 389* (30, $M^+ - C_4H_9$), 333* (40.5), 235* (16.5), 179* (29), 121* (10.5), 73 (100).

30a. ^1H NMR: 6.60 (s, 1 H, $^3J_{SnH}$ = 118 Hz), 6.08 (s, 1 H, $^3J_{SnH}$ = 58 Hz), 2.22 (s, 3 H). GC/MS: 303* (100, $M^+ - C_4H_9$), 247* (11), 189* (35), 119 (11). IR (neat): 1668 cm^{-1}.

32a. ^1H NMR: 7.50 (d, J = 20 Hz, 1 H), 6.46 (d, J = 20 Hz, 1 H), 2.20 (s, 3 H). GC/MS: 305* (100, $M^+ - C_4H_9$), 247* (11.5), 189* (36), 119 (11).

30b. ^1H NMR: 5.68 (t, J = 7.5 Hz, 1 H, $^3J(^{117}SnH)$ = 62.5 Hz, $^3J(^{119}SnH)$ = 65.5 Hz), 2.20 (s, 3 H), 2.20–2.10 (m, 2 H). GC/MS: 387* (100, $M^+ - C_4H_9$), 271* (7), 177* (8), 137* (7), 43 (10), 41 (11).

30c. ^1H NMR: 7.94 (m, 2 H) and 7.58–7.32 (m, 3 H), 5.94 (t, J = 7 Hz, 1 H, $^3J(^{117}SnH)$ = 60.5 Hz, $^3J(^{119}SnH)$ = 63 Hz), 2.01 (dt, J = 7 Hz, 2 H). **31c.** ^1H NMR: 7.79 (m, 2 H) and 7.58–7.32 (m, 3 H), 6.69 (t, J = 7 Hz, 1 H, $^3J_{SnH}$ = 130 Hz), 2.26 (dt, J = 7 Hz, 2 H).

30d. ^1H NMR: 6.90 (d, J = 3 Hz, 1 H, $^3J(^{117}SnH)$ = 107 Hz, $^3J(^{119}SnH)$ = 112 Hz), 5.93 (d, J = 3 Hz, 1 H, $^3J(^{117}SnH)$ = 52 Hz, $^3J(^{119}SnH)$ = 54 Hz), 3.73 (s, 3 H). GC/MS: 303* (100, $M^+ - C_4H_9$), 247* (6), 189* (18), 119 (9). Anal. Calcd for $C_{16}H_{32}O_2Sn$: C, 51.23; H, 8.60. Found: C, 51.17; H, 8.74.

30e. ^1H NMR: 6.06 (t, J = 7 Hz, 1 H, $^3J_{SnH}$ = 60 Hz), 4.15 (q, J = 7 Hz, 2 H), 2.45 (dt, J = 7 and 7.5 Hz, 2 H). GC/MS: 389* (100, $M^+ - C_4H_9$), 343* (30), 341* (30), 179* (23), 163* (13), 121 (14), 41 (11). IR (neat): 1714 cm^{-1}. **32e.** ^1H NMR: 5.94 (s, 1 H, $^3J_{SnH}$ = 68 Hz), 4.15 (q, J = 7 Hz, 2 H), 2.89 (t, J = 7 Hz, 2 H, $^3J_{SnH}$ = 58 Hz). GC/MS: 389* (100), 333* (25), 177* (18), 165* (17), 121* (20), 81 (13). IR (neat): 1720 cm^{-1}.

30f. ^1H NMR: 6.08 (t, J = 7 Hz, 1 H, $^3J_{SnH}$ = 60 Hz), 6.30–5.80 (m, 1 H, $CO_2CH_2CH{=}CH_2$), 5.39–5.18 (m, 2 H, $CO_2CH_2CH{=}CH_2$), 4.60 (m, 2 H, $CO_2CH_2CH{=}CH_2$), 2.44 (dt, J = 7 and 7.5 Hz, 2 H). GC/MS: 401* (100, $M^+ - C_4H_9$), 343* (37), 289* (11), 231* (9), 177* (35), 121* (11), 41 (10). IR (neat): 1715 cm^{-1}. **32f.** ^1H NMR: 5.97 (s, 1 H), 6.30–5.80 (m, 1 H), 5.40–5.19 (m, 2 H), 4.60 (m, 2 H), 2.90 (t, J = 7 Hz, 2 H, $^3J_{SnH}$ = 57 Hz). IR (neat: 1720 cm^{-1}. GC/MS: 401* (100, $M^+ - C_4H_9$), 345* (21), 289* (12), 177* (21), 121* (113), 41 (11).

30g. ^1H NMR: 6.66 (s, 1 H, $^3J(^{117}SnH)$ = 84 Hz, $^3J(^{119}SnH)$ = 88 Hze, 4.18 (q, J = 7.5 Hz, 2 H), 0.07 (s, 9 H). GC/MS: 447* (4.2, $M^+ - CH_3$), 405 (100, $M^+ - C_4H_9$), 361* (38), 305* (10), 247* (18), 235* (14), 219* (11), 179* (46), 121* (23), 113 (15), 73 (35), 41 (11). IR (neat): 1712 cm^{-1}. Anal. Calcd for $C_{20}H_{42}O_2SiSn$: C, 52.07; H, 9.18. Found: C, 52.33; H, 9.03.

30i. ^1H NMR: 7.32–7.18 and 6.93 (m, 5 H), 5.88 (q, J = 7 Hz, $^3J(^{117}SnH)$ = 63 Hz, $^3J(^{119}Sn)$ = 67 Hz. 1.67 (d, J = 7 Hz, 3 H). GC/MS: 351* (100, $M^+ - C_4H_9$), 295* (44), 237* (70), 197* (20), 179* (19), 177* (23), 121* (35), 117 (53), 115 (36), 91 (22). Anal. Calcd for $C_{21}H_{36}Sn$: C, 61.94; H, 8.91. Found: C, 61.69; H, 9.11. **32i.** ^1H NMR: 7.40–7.05 (m, 5 H), 6.60 (q, J = 2 Hz, $^3J_{SnH}$ = 70

(56) Seyferth, D.; Vik, S. C. *J. Organomet. Chem.* **1978**, *144*, 1.

Hz), 2.12 (d, J = 2 Hz, 3 H, $^3J_{SnH}$ = 49 Hz). GC/MS: 351* (100, $M^+ - C_4H_9$), 293* (37), 237* (54), 197* (17), 179* (17), 177* (18), 121* (23), 117 (27), 115 (13).

30j. ^{1}H NMR: 7.48–7.11 (m, 5 H), 6.03 (d, J = 2 Hz, 1 H, $^3J(^{117}SnH)$ = 125 Hz, $^3J(^{119}SnH)$ = 131 Hz), 5.42 (d, J = 2 Hz, $^3J(^{117}SnH)$ = 60 Hz, $^3J(^{119}SnH)$ = 62 Hz). GC/MS: 337* (100, $M^+ - C_4H_9$), 223* (55), 197* (25), 121* (15). **32j.** ^{1}H NMR: 7.78–7.11 (m, 5 H), 6.87 (s, 2 H, J_{SnH} = 66 Hz). GC/MS: 337* (100, $M^+ - C_4H_9$), 223* (68), 197* (28), 121* (23), 41 (19).

26. ^{1}H NMR: 5.77 (t, J = 7.0 Hz, 1 H, $^3J_{SnH}$ = 32 Hz), 2.30 (dt, J = 7 and 7.5 Hz, 2 H). GC/MS: 380* (3.5, $M^+ - C_4H_8$), 379* (3, $M^+ - C_4H_9$), 345* (0.6 $M^+ - C_4H_8$, - Cl), 344* (0.6, $M^+ - C_4H_9$, - Cl), 323* (0.9), 290* (0.9), 269* (100), 213* (18), 177* (18), 155* (12), 57 (24), 41 (31). Anal. Calcd for $C_{20}H_{41}ClSn$: C, 55.14; H, 9.49; Cl, 8.17. Found: C, 55.34; H, 9.18; Cl, 7.93.

39. ^{1}H NMR: 5.82 (t, J = 7 Hz, 1 H, $^3J_{SnH}$ = 57 Hz), 2.37 (m, 4 H, CH_2—═ and CH_2—≡). GC/MS: 545* (0.6, M^+), 397* (100, $M^+ - C_4H_9$), 235* (7), 179* (16), 177* (27), 117* (8), 91 (12), 79 (15), 55 (10), 41 (15). ^{13}C NMR: 151.35, 123.2, 98.3, 81.9, 32.4, 31.35, 31.3, 29.0 O (3 C), 27.8, 27.3 (3 C) 22.3, 21.9, 19.7, 14.0 13.7 (3 C), 9.9 (3C).

42. ^{1}H NMR: 6.13 (d, J = 3.5 Hz, 1 H, $^3J(^{117}SnH)$ = 114 Hz, $^3J(^{119}SnH)$ = 122 Hz), 5.45 (d, J = 3.5 Hz, 1 H, $^3J_{SnH}$ = 55 Hz), 2.35 (t, J = 6.5 Hz, 2 H). GC/MS: 369* (100, M^+ - 57), 291* (13), 257* (24), 255* (32), 253* (22), 235* (26), 227* (8), 179* (57), 177* (94), 175* (67), 123* (14), 121* (48), 120* (23), 79 (11), 65 (22), 41 (34). ^{13}C NMR: 135.05, 133.8, 95.6, 84.25, 31.4, 29.05, 28.9 (3 C), 28.65, 27.3 (3 C), 22.6, 19.9, 14.1, 13.7 (3C) 10.05 (3 C).

43. ^{1}H NMR: 5.83 (t, J = 7 Hz, 1 H, $^3J_{SnH}$ = 55 Hz), 2.35 (dt, J = 7 and 7.5 Hz), 0.11 (s, 9 H). GC/MS: 441* (100, $M^+ - C_4H_9$), 385* (3.35) , 327* (20), 329* (19), 227* (12), 179* (16), 177* (20), 135* (13), 121* (19), 73 (62), 41 (13). IR (neat): 2130 cm^{-1}. Anal. Calcd for $C_{25}H_{50}SiSn$: C, 60.36; H, 10.13. Found: C, 60.30; H, 9.90.

(*E*)-2-Hydroxy-3-(tributylstannyl)-3-decene (33) from 3-decyn-2-one (29b). A 320-mg portion of tributyltin hydride (1.1 mmol) was added dropwise to a solution of 152 mg of 3-decyn-2-one (1 mmol) and 14 mg (0.02 mmol) of $PdCl_2(PPh_3)_2$ in 4 mL of THF. Stirring was continued for 10 min. Then the THF was evaporated on a vacuum line and replaced by 6 mL of diethyl ether. The reaction mixture was cooled to −78 °C, and 1.2 mL of a 1 M commercial solution of DIBAL in hexane was added by a syringe over a period of 5 min. The reaction mixture was then allowed to warm to room temperature for 30 min, after which 2 mL of methanol followed by 5 mL of benzene and 2 mL of water was added. The precipitated aluminium salts were filtered and washed throughly with methanol. The combined filtrate and washings were evaporated, and the residue was purified by column chromatography (silica gel; AcOEt/hexane, 1/6) to give 271 mg of **3**. Yield: 61% colorless oil. ^{1}H NMR: 5.44 (dt, $^4J_{HH}$ = 1.5 Hz, $^3J_{HH}$ = 7 Hz, 1 H, $^3J_{SnT}$ = 71 Hz), 4.81 (dq, J = 1.5 and 7 Hz, 1 H, $^3J_{SnH}$ = 66 Hz), 2.18–1.93 (m, 2 H, allylic H). Anal. Calcd for $C_{22}H_{46}OSn$: C, 59.24; H, 10.41. Found: C, 59.54; H, 10.24.

(*E*)-1-Bromo-1-chloro-1-octene (27). A solution of 119 mg (0.274 mmol) of (*E*)-1-(tributylstannyl)-1-chloro-1-octene in dichloromethane (6 mL) was cooled to −78 °C under argon atmosphere. While stirring, a solution of 44 mg of bromine in 2 mL of dichloromethane was added slowly by syringe over a period of 45 min.[57] The reaction mixture was allowed to warm to room temperature for 30 min. Workup and purification were carried out as described for (*E*)-1-iodo-1-chloro-1-octene (see below). Yield in **27**: 56 mg (90%). Colorless oil. ^{1}H NMR: 6.10 (t, J = 7 Hz, 1 H), 2.14 (q, J = 7 Hz, 2 H), 1.48–1.20 (m, 8 H), 0.89 (t, J = 7 Hz, 3 H). GC/MS: 228, 226, 224 (0.42, 1.67, 1.25, M^+), 157, 155, 153 (2.08, 8.96, 6.46, $M^+ - C_5H_{11}$), 109 (31), 75 (101), 69 (25), 67 (33), 56 (44), 43 (100). ^{13}C NMR: 135.2, 103.7, 31.5, 30.5, 28.7, 27.95, 22.5, 14.05.

(*E*)-1-Iodo-1-chloro-1-octene (28). A solution of 76.2 mg of iodine (0.3 mmol) in dichloromethane (2 mL) was syringed, over a period of 30 min, into a stirred solution of 130.5 mg (0.3 mmol) of (*E*)-1-(tributylstannyl)-1-chloro-1-octene in 6.5 mL of dichloromethane maintained at 0 °C and under argon atmosphere.[57] The reaction mixture was then allowed to warm to room temperature for 30 min. It was then washed twice with aqueous sodium bisulfite (10%) and then once with 5 mL of a 10% aqueous solution of potassium fluoride to convert tributyltin iodide into tributyltin fluoride.[58] The insoluble tributyltin fluoride was eliminated by filtration, and the organic phase was decanted and dried over magnesium sulfate. After evaporation of dichloromethane by rotary evaporator, the residue was purified by short column chromatography (silica gel, hexane) to give 68 mg (83%) of pure (*E*)-1-iodo-1-chloro-1-octene. Colorless oil. ^{1}H NMR: 6.43 (t, J = 7 Hz, 1 H), 2.15 (q, J = 7 Hz, 2 H), 1.48–1.20 (m, 8 H), 0.89 (t, J = 7 Hz, 3 H). GC/MS: 274, 272 (1.41, 4.22, M^+), 203, 201 (4.92, 14.05, $M^+ - C_5H_{11}$), 190, 188 (3.5, 10.3), 109 (26), 83 (16), 75 (18), 69 (26), 67 (75), 56 (35), 55 (56), 53 (18), 43 (100). ^{13}C NMR: 144.4, 66.2, 31.7, 31.05, 28.7, 27.9, 22.5, 14.0.

2,3-Dicarbomethoxy-1,3-butadiene (37a). Via the procedure of Kyler and co-workers,[6] methyl 2-(tributylstannyl)propenoate (**30d**) (375 mg, 1 mmol) was added in one portion to a solution of 242 mg of $Cu(NO_3)_2 \cdot 3H_2O$ (1 mmol) in 1 mL of THF. The reaction mixture was stirred for 10 min at room temperature. It was then diluted with 75 mL of ethyl acetate and washed successively with 50 mL of 5% aqueous ammonia, 50 mL of water, and 50 mL of brine. The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude residue was directly analyzed by NMR. ^{1}H NMR: 6.29 (d, J = 2 Hz, 2 H), 5.81 (d, J = 2 Hz, 2 H), 3.77 (s, 6 H). Analytical yield (anisole as the NMR reference): 58%. No other NMR signals could be detected in the 10.0–2.0 ppm region. Loss of product is thus likely to be due to a competitive protodestannylation, induced by $Cu(NO_3)_2 \cdot 3H_2O$, of **30d** to the volatile methyl propenoate.

1-Hydroxy-2-(tributylstannyl)-2-propene (Scheme III). A solution of 17.31 g (46.4 mmol) of methyl 2-(tributylstannyl)-propenoate in 50 mL of diethyl ether was cooled to −78 °C under argon atmosphere. To this stirred solution, 97 mL of a 1 M solution of diisobutylaluminium hydride in hexane was added slowly by syringe. The reaction mixture was stirred overnight at room temperature; 10 mL of methanol was then added, followed by 5 mL of water and 50 mL of benzene. The precipitated aluminium salt was removed by filtration and washed with methanol. The combined filtrate and washing were evaporated in vacuo to give 13.6 g (85%) of crude 1-hydroxy-2-(tributylstannyl)-2-propene.

1-Acetoxy-2-(tributylstannyl)-2-propene (Scheme III). The crude alcohol (13.6 g, 40 mmol) and 0.48 g of 4-(dimethylamino)pyridine (40 mmol) were dissolved in dry pyridine (10 mL). The solution was cooled to 0 °C and stirred while 6.12 g of acetic anhydride were added over 15 min. The reaction mixture was further stirred for 4 h at room temperature. Pyridine was evaporated in vacuo, and the residue was purified by column chromatography (silica gel; EtOAc/cyclohexane, 1/23); 7.83 g of pure acetate (51% yield) was obtained as a colorless oil. ^{1}H NMR: 5.88 (t, J = 2 Hz, 1 H, $^3J_{SnH}$ = 124 Hz), 5.31 (t, J = 2 Hz, 1 H, $^3J_{SnH}$ = 60 Hz), 4.72 (m, 2 H, $^3J_{SnH}$ = 30 Hz)e, 2.09 (s, 3 H). GC/MS: 333*/(50, $M^+ - C_4H_9$), 293* (100), 233* (14), 179* (68), 137* (11), 121* (17), 57 (13), 41 (13).

2-[2-(Tributylstannyl)propen-2-yl]malonic Acid Bis(methyl ester) (Scheme III). A 0.9-g portion of sodium hydride 60% in mineral oil (25 hydride mequiv) was washed free of mineral oil with pentane and covered with ca. 100 mL of dry THF. The resulting heterogeneous mixture was stirred under argon and cooled to 0 °C, and dimethyl malonate (2.64 g, 20 mmol) was added over a period of 10 min. Stirring was continued at room temperature until gas evolution ceased, and then the excess of sodium hydride was allowed to decant. Acidimetric titration, performed on an aliquot of supernatant, gave a 0.185 M concn. in the sodium salt of dimethyl malonate.

A Schlenk tube charged with 3.89 g (10 mmol) of 1-acetoxy-2-(tributylstannyl)-2-propene, 262 mg of triphenylphosphine (1 mmol), and 577 mg (0.5 mmol) of $Pd(PPh_3)_4$ was filled with argon; 20 mL of degassed THF was then added. To this solution, cooled to 0 °C was added 54 mL of the 0.185 M THF solution of dimethyl

(57) To avoid any isomerization of (*E*)-1-bromo-1-chloro-1-octene or (*E*)-1-iodo-1-chloro-1-octene to the *Z* isomers, we found it imperative to carry out the addition of Br_2 or I_2 slowly, at low temperature, and under high dilution as described here.

(58) Harpp, D. N.; Gongras, M. *J. Am. Chem. Soc.* **1988**, *110*, 7737 and references therein.

malonate sodium salt (10 mmol) over a few minutes. The reaction mixture was stirred for an additional 6 h at room temperature. THF was then evaporated in vacuo. Standard workup procedure (diethyl ether/water), followed by column chromatography (silica gel; EtOAc/cyclohexane, 1/11) gave 4.0 g (87% yield) of 2-[2-(tributylstannyl)propen-2-yl]malonic acid bis(methyl ester). Colorless oil. ^{1}H NMR: 5.71 (d, $^2J_{HH}$ = 1 Hz, 1 H, $^3J_{SnH}$ = 132 Hz), 5.18 (m, 1 H, $^3J_{SnH}$ = 61 Hz), 3.72 (s, (3 + 3) H), 3.54 (t, J = 7.5 Hz, 1 H), 2.84 (broad d, J = 7.5 Hz, 2 H, $^3J_{SnH}$ = 40 Hz.

2-[2-(Tributylstannyl)propen-2-yl]-2-(2-bromopropen-2-yl)malonic Acid Bis(methyl ester) (Scheme II). In a Schlenk tube, 3 mequiv of sodium hydride, cleansed of oil as described above, was suspended in 15 mL of THF under argon atmosphere. This slurry was cooled at 0 °C and stirred while 922 mg of 2-[2-(tributylstannyl)propen-2-yl]malonic acid bis(methyl ester) (2 mmol) was added over a few minutes. The cooling bath was removed, and the reaction mixture was stirred for 30 min. The excess of sodium hydride was decanted, and the supernatant was transferred into a second Schlenk tube via a stainless-steel double-ended needle. Sodium hydride was washed with an additional 5 mL of THF and decanted, and the THF washing was also transferred to the second Schlenk tube. To this homogeneous solution, 1,2-dibromo-2-propene (600 mg, 3 mmol) was added, and the reaction mixture was stirred overnight at room temperature. Standard workup procedure (diethyl ether–water) followed by column chromatography (silica gel; AcOEt/cyclohexane, 1/11) gave 853 mg (74%) of 2-[2-(tributylstannyl)propen-2-yl]-2-(2-bromopropen-2-yl)malonic acid bis(methyl ester). Colorless oil. ^{1}H NMR: 5.66 (sharp m, 1 H, *H*C=CBr), 5.64 (broad s, 1 h, $^3J_{SnH}$ = 137 Hze, 5.55 (sharp m, *H*C=CBr), 5.23 (broad s, 1 H, $^3J_{SN}$ = 65 Hze, 3.71 (s, (3 + 3) H), 3.25 (broad s, 2 H), 2.91 (m, 2 H, $^3J_{snH}$ = 37 Hz).

1,1-Dicarbomethoxy-3,4-bis(methylidene)cyclopentane (37b). A 200-mg (0.5-mmol) sample of the preceding compound was dissolved in 2 mL of DMF. The solution was degassed on a vacuum line, and 7 mg of $PdCl_2(CH_3CN)_2$ (0.05 equiv) were rapidly added under a slow streat of argon. The solution was degassed once more and stirred for 20 h at room temperature under argon atmosphere; 2 mL of saturated aqueous sodium bicarbonate was then added, and the aqueous mixture was extracted with 4 mL of a 1/1 (v/v) mixture of hexane and ethyl acetate. The organic phase was washed twice with 10 mL of water and dried over magnesium sulfate. The solvent was evaporated, and the residue was purified by column chromatography (silica gel; EtOAc/cyclohexane, 1/10) to give 69 mg (66% yield) of **37b**. Colorless oil. ^{1}H NMR: 5.41 (m, 2 H) and 4.97 (m, 2 H), vinylic H), 3.74 (s, (3 + 3) H), 3.05 (m, 4 H). Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.59; H, 6.84.

Acknowledgment. We are grateful to Dr. G. Linstrumelle and Dr. R. Lett for very helpful discussions.

Note Added in Proof. Very recently, the palladium-catalyzed hydrostannation of alkynes and especially of conjugated alkynoic esters has been independently described by Cochran and co-workers.[59,60] The regiochemical outcome and the stereochemical outcome of these reactions are essentially the same as those reported here with tributyltin hydride. The apparent discrepancy between the two results (see footnote 28 in ref 59) is due to a misprint in our preliminary communication (see ref 18 and its corrigendum).

Registry No. **1**, 13965-03-2; **3**, 33221-76-0; **5a**, 110-65-6; **5b**, 1942-45-6; **5c**, 73252-74-1; **6a**, 103223-42-3; **6b**, 124602-63-7; **6ca**, 124582-28-1; **6cb**, 124582-29-2; **7a**, 107-19-7; **7b**, 13610-02-1; **7c**, 6089-04-9; **7d**, 7223-38-3; **7e**, 2028-63-9; **7f**, 115-19-5; **7g**, 818-72-4; **7h**, 60134-93-2; **7i**, 4187-87-5; **7j**, 629-05-0; **7k**, 693-02-7; **7l**, 124582-19-0; **8a**, 84666-30-8; **8b**, 119649-70-6; **8c**, 119649-67-1; **8d**, 122229-79-2; **8e**, 107352-75-0; **8f**, 87836-16-6; **8g**, 116854-44-5; **8h**, 124582-21-4; **8i**, 124582-22-5; **8j**, 124582-24-7; **8k**, 122229-77-0; **8l**, 124582-26-9; **9a**, 74141-12-1; **9b**, 119649-71-7; **9c**, 55723-10-9; **9d**, 124582-20-3; **9e**, 107352-74-9; **9f**, 79970-78-8; **9g**, 79970-81-3; **9h**, 124648-33-5; **9i**, 124582-23-6; **9j**, 67693-83-8; **9k**, 124582-25-8; **9l**, 124582-27-0; **12**, 12245-55-5; **13**, 33135-96-5; **14**, 40691-33-6; **15**, 30153-54-9; **16a**, 927-80-0; **16b**, 1066-54-2; **16c**, 3844-94-8; **16d**, 14630-40-1; **16e**, 35864-20-1; **17a**, 97674-02-7; **17b**, 121052-02-6; **17c**, 124582-31-6; **18a**, 124582-30-5; **18b**, 58207-97-9; **18c**, 124582-32-7; **25**, 64531-26-6; **26**, 124582-46-3; **27**, 124582-50-9; **28**, 124582-51-0; **29a**, 1423-60-5; **29b**, 91658-50-3; **29c**, 18998-78-2; **29d**, 922-67-8; **29e**, 16930-95-3; **29f**, 124582-44-1; **29g**, 16205-84-8; **29h**, 5930-98-3; **29i**, 673-32-5; **29j**, 536-74-3; **30a**, 124582-33-8; **30b**, 124582-34-9; **30c**, 124582-35-0; **30d**, 124582-37-2; **30e**, 124582-38-3; **30f**, 124582-40-7; **30g**, 124582-42-9; **30i**, 112713-91-4; **30j**, 92074-28-7; **31c**, 124582-36-1; **32a**, 94806-25-4; **32e**, 124582-39-4; **32f**, 124582-41-8; **32i**, 124582-43-0; **32j**, 66680-88-4; **33**, 124582-45-2; **36**, 38818-30-3; **37**, 87185-05-5; **38**, 1120-29-2; **39**, 124582-47-4; **40**, 55682-66-1; **41**, 84751-17-7; **42**, 124582-48-5; **43**, 124582-49-6; **56**, 121051-99-8; Na_2PdCl_4, 13820-53-6; P(*o*-tolyl)$_3$, 6163-58-2; $(EtO)_2P(O)Cl$, 814-49-3; $(EtO)_2P(O)OCH_2C{\equiv}CH$, 17118-80-8; $PdCl_2(CH_3CN)_2$, 14592-56-4; Bu_3SnH, 688-73-3; $CH_2{=}CH(SnBu_3)CH_2CH(CO_2Me)_2$, 124582-52-1; $BrCH_2C(Br){=}CH_2$, 513-31-5; $CH_2{=}C(SnBu_3)CH_2C(CO_2Me)_2CH_2C(Br){=}CH_2$, 124582-53-2.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for new compounds described in this paper (40 pages). Ordering information is given on any current masthead page.

(59) Cochran, J. C.; Williams, L. E.; Bronk, B. S.; Calhoun, J. A.; Fassberg, J.; Clark, K. J. *Organometallics* **1989**, *8*, 804.

(60) Cochran, J. C.; Bronk, B. S.; Terence, X. M.; Phillips, H. K. *Carbonyl Substituted Vinylstannanes: Preparation and Protodestannylation*; reported at the Sixth International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin, and Lead, July 23–28, 1989, Brussels, Belgium.