Application of Fluoride-Catalyzed Silane Reductions of Tin Halides to the in Situ Preparation of Vinylstannanes

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We have found that either $Bu_3SnCl/PMHS/KF_{(aq)}$ or the combination of tributyltin fluoride, PMHS, and catalytic quantities of tetrabutylammonium fluoride can serve as in situ sources of tributyltin hydride for both free radical and palladium-catalyzed hydrostannylation reactions. These methods are tolerant of a variety of functional groups, including silyl ethers. Furthermore, Me_3SnCl is also reduced under these conditions, providing a relatively convenient and safe manner by which Me_3SnH can be formed and reacted. We have also observed that the Bu_3SnCl/siloxane/fluoride combination offers improvements over the existing protocols for transforming 1-bromoalkynes into *trans*-1-(tributylstannyl)-1-alkenes. Specifically, the KF/PMHS methodology allows the 1-bromoalkyne to be formed and reacted in a single pot and with substoichiometric amounts of tin. Finally, alternative reductants such as Red-Sil are also amenable to the method.

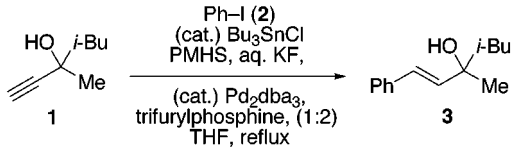
Introduction

We recently reported[1] on the generation of tributyltin hydride via reduction of tributyltin chloride by hypervalent polymethylhydrosiloxane (PMHS + potassium fluoride).[2,3,4] This methodology allows for the employment of substoichiometric amounts of tin hydride in a variety of chemical processes, including free radical reactions of aliphatic and aromatic halides and palladium-catalyzed reductions of α,β-unsaturated aldehydes. As part of this early study, we also demonstrated that the combination of PMHS, aqueous KF, and catalytic Bu_3SnCl in the presence of an alkyne, catalytic Pd_2dba_3/TFP, and iodobenzene could effect an initial palladium-catalyzed hydrostannylation, followed by a subsequent Stille cross-coupling of the in situ formed vinylstannane (Scheme 1).[1,5] However, given both the transient nature of the vinylstannanes and the relatively low yields observed in these reactions, we were uncertain as to the overall efficiency of employing $Bu_3SnCl/PMHS/KF_{(aq)}$ as an in situ source of tributyltin hydride in preparative[3a,b] hydrostannylation reactions.

Results and Discussion

Part of this investigation has focused on gaining a fuller understanding of the application of siloxane reductions of tin halides to the in situ hydrostannylation of alkynes. Drawing on our experience with one-pot hydrostannylation/Stille couplings, we first focused on palladium-mediated hydrostannylations.[6] We were initially disappointed when the reactions of several 1-alkynes[7] with Bu_3SnCl, aqueous KF, and PMHS in THF proved inconsistent. Although the anticipated vinyltins were produced, yields and purity levels were usually low.[8] However, after some experimentation, we found that by

Scheme 1



Bu_3SnCl [mol%]	{Pd} [mol%]	Sn-turnovers	[%] yield
10	1	2	19
6	0.2	2.5	15
6	0.4	3	21

(1) Terstiege, I.; Maleczka, R. E., Jr. *J. Org. Chem.* **1999**, *64*, 342−343.

(2) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371−1448.

(3) For other methods of generating trialkyltin hydrides, see: (a) *Chemistry of Tin*; Smith, P. J., Ed.; Blackie Academic & Professional: New York, 1998. (b) Pereyre, M.; Quintard, J.-P.; Rahm, A. In *Tin in Organic Synthesis*; Butterworth: Toronto, 1987. Via PMHS reduction of tin oxides: (c) Hayashi, K.; Iyoda, J.; Shiihara, I. *J. Organomet. Chem.* **1967**, *10*, 81−94. (d) Corey, E. J.; Wollenberg, R. H. *J. Org. Chem.* **1975**, *40*, 2265−2266. (e) Hays, D. S.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 2796−2797. Via silane reduction of tin amides: (f) Hays, D. S.; Fu, G. C. *J. Org. Chem.* **1997**, *62*, 7070−7071.

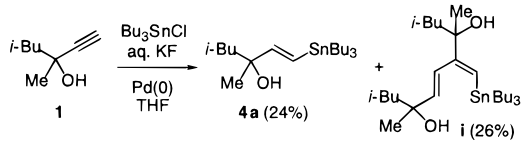
(4) For a general discussion of PMHS-based reductions see Mimoun, H. *J. Org. Chem.* **1999**, *64*, 2582−2589 and references therein.

(5) Maleczka, R. E., Jr.; Terstiege, I. *J. Org. Chem.* **1998**, *63*, 9622−9623.

(6) (a) Kikukawa, K.; Umekawa, H.; Wada, F.; Matsuda, T. *Chem. Lett.* **1988**, 881−884. (b) Zhang, H. X.; Guibé, F.; Balavoine, G. *Tetrahedron Lett.* **1988**, *29*, 619−622. (c) Zhang, H. X.; Guibé, F.; Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1857−1867.

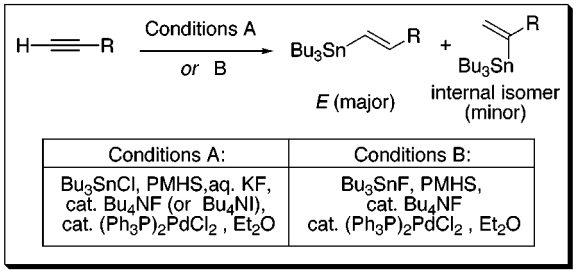
(7) All starting 1-alkynes were purchased from Aldrich except (a) 5-(*tert*-butyldimethylsilyloxy)-1-pentyne (**11**) (Marshall, J. A.; DeHoff, B. S. *J. Org. Chem.* **1986**, *51*, 863−872), (b) 6-(*tert*-butyldimethylsilyloxy)-1-hexyne (**13**) (Kalivretenos, A.; Stille, J. K.; Hegedus, L. S. *J. Org. Chem.* **1991**, *56*, 2883−2894), (c) 6-aceto-1-hexyne (**19**) (Sharma, S.; Oehlschlager, A. C. *J. Org. Chem.* **1989**, *54*, 5064−5073), and (d) 5-(tetrahydropyranyloxy)-1-pentyne (**27**) (Hutzinger, M. W.; Oehlschlager, A. C. *J. Org. Chem.* **1995**, *60*, 4595−4601), which were prepared by the methods cited above.

(8) Though not consistently reproducible, reactions run in THF produce stannyldienes with proposed structure **i** in yields as high as 26%. For further details, including the structure elucidation of **i**, please see the Supporting Information.

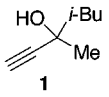
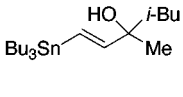
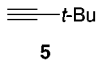
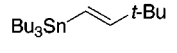
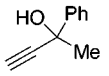
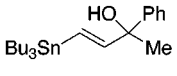
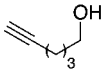
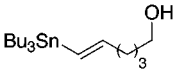
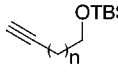
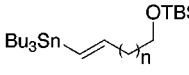
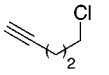
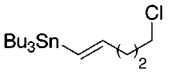
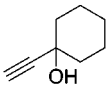
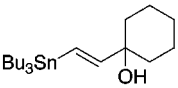


10.1021/jo990491+ CCC: $18.00
Published on Web 07/14/1999

Scheme 2

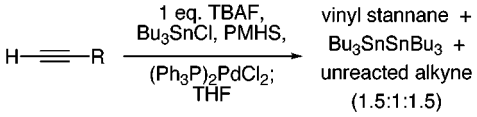


Conditions A:	Conditions B:
Bu_3SnCl, PMHS,aq. KF, cat. Bu_4NF (or Bu_4NI), cat. $(Ph_3P)_2PdCl_2$, Et_2O	Bu_3SnF, PMHS, cat. Bu_4NF cat. $(Ph_3P)_2PdCl_2$, Et_2O

alkyne	product	yields Conditions A	yields Conditions B
 **1**		66% *E*/int. (24:1) **4a/4b**	67% *E*/int. (21:1) **4a/4b**
 **5**		59% *E*/int. (>99:1) **6**	67% *E*/int. (>99:1) **6**
 **7**		86% *E*/int. (12:1) **8a/8b**	68% *E*/int. (>99:1) **8a/8b**
 **9**		72% *E*/int. (1.4:1) **10a/10b**	77% *E*/int. (1.4:1) **10a/10b**
 **11** (n=2) **13** (n=3)		51% (n=2) *E*/int. (1:1) **12a/12b**	53% (n=3) *E*/int. (1.3:1) **14a/14b**
 **15**		84% *E*/int. (1.4:1) **16a/16b**	78% *E*/int. (1.4:1) **16a/16b**
 **17**		62% *E*/int. (17:1) **18a/18b**	70% *E*/int. (>99:1) **18a/18b**

using Et_2O as the solvent and including a catalytic amount of tetrabutylammonium fluoride (TBAF) or iodide (TBAI)[9] in the reaction, the expected vinylstannanes were formed in good yields and with standard regiochemical outcomes[10] (Scheme 2; conditions A[7,11]). Importantly, potentially reactive groups such as alkyl halides or silyl ethers[12] remained intact throughout the reaction sequence. Furthermore, we observed no evidence of palladium-mediated hydrosilylation by the PMHS. Although the hydrostannylations with $Bu_3SnCl/PMHS/KF_{(aq)}$ proved similar in many regards to those carried out with pre-made Bu_3SnH, there were several significant differences.

Scheme 3



For example, palladium-catalyzed hydrostannylations using Bu_3SnH directly are often complicated by the palladium-promoted conversion of Bu_3SnH into $Bu_3SnSnBu_3$.[13] Under the $Bu_3SnCl/PMHS/KF_{(aq)}$ conditions, the vinylstannanes are accompanied by little if any hexabutylditin byproduct. Presumably, the rates of tin hydride formation and hydrostannylation are such that the relative concentration of tin hydride is always low, thereby minimizing dimer formation. This phenomena can be of particular practical advantage when vinyltins are desired in quantities that dissuade their distillation and when they are also sufficiently nonpolar so as to make the chromatographic separation from the ditin difficult.

In terms of solvent, an obvious difference between our method and traditional hydrostannylations is the inclusion of water in the reaction. Although the advantages of running organic reactions in water have been well documented,[14] we also recognized that a more anhydrous variant of our protocol would have its own advantages. Toward this aim, we examined the potential of KF or CsF in anhydrous ether to serve as sources of fluoride for our reaction. Unfortunately, under such conditions little or no vinyltins were generated. Given our observation that the biphasic reactions were facilitated by the presence of catalytic amounts of TBAF, we decided to explore its use in stoichiometric quantities. Employing 1 equiv of TBAF did result in complete and rapid generation of Bu_3SnH; however, the subsequent hydrostannylation did not go to completion, as the reaction afforded a 1:1 ratio of vinylstannane and unreacted alkyne, along with a 50% yield of hexabutylditin (Scheme 3). This result was not entirely unexpected as tetrabutylammonium salts are known to greatly activate the Sn−H bond, leading to hydrogen gas evolution and ditin formation.[15] The presence of $Bu_3SnSnBu_3$ and product were evidence that TBAF could serve to activate PMHS[2] and thus generate Bu_3SnH; however, it was also clear that we would have to minimize the TBAF concentration if we wished for the tin hydride to be available for hydrostannylation versus dimer formation. However, treatment of terminal alkynes with Bu_3SnCl, PMHS, and catalytic TBAF in the absence of KF also failed to provide any vinylstannane. Presumably the TBAF is reacting with the Bu_3SnCl to form Bu_3SnF and thereby not allowing for the activation of the PMHS.[16] Assuming this were the case, we rationalized that by using pre-made Bu_3SnF as the starting material the reaction could be made catalytic with respect to the TBAF, because a fluoride anion would be regenerated

(9) Although successful, reactions carried out in the absence of TBAF or TBAI ran considerably slower.

(10) The reported ratios of vinyltin isomers were based on isolated material. These ratios occasionally differed slightly from those taken (^{1}H NMR) from the crude mixture, presumably as a result in part of protiodestannylation during silica gel chromatographic purification (see: Hitchcock, S. A.; Mayhugh, D. R.; Gregory, G. S. *Tetrahedron Lett.* **1995**, *36*, 9085−9088 and ref 6c).

(11) CsF may be substituted for KF with little change in the outcome of the reaction.

(12) Some substrate intolerance was observed when 6-(*tert*-butyldimethylsilyloxy)-1-hexyne (**13**) was subjected to conditions A. In this case, although the TBS group remained in place, a significant amount of destannylation occurred.

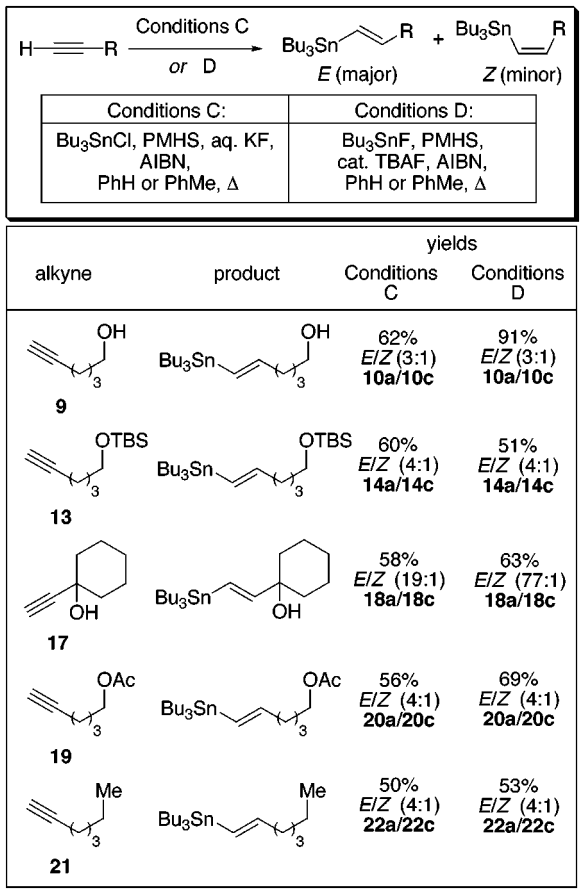
(13) Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1986**, *304*, 257−265.

(14) (a) Lubineau, A.; Augé, J.; Queneau, Y. *Synthesis* **1994**, 741−760. (b) Chan, T. H.; Li, C. J.; Lee, M. C.; Wei, Z. Y. *Can. J. Chem.* **1994**, *72*, 1181−1192. (c) Li, C.-J. *Chem. Rev.* **1993**, *93*, 2023−2035. (d) Grieco, P. A. *Aldrichimica Acta* **1991**, *24*, 59−66. (e) Breslow, R. *Acc. Chem. Res.* **1991**, *6*, 159−164.

(15) Kawakami, T.; Shibata, I.; Baba, A. *J. Org. Chem.* **1996**, *61*, 82−87.

(16) Preliminary ^{119}Sn NMR data is consistent with this hypothesis, as is literature precedent, see: Leibner, J. E.; Jacobus, J. *J. Org. Chem.* **1979**, *44*, 449−450.

Scheme 4

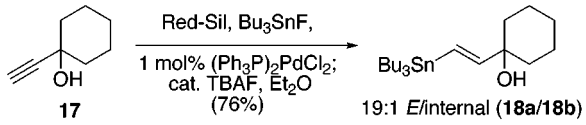


upon the PMHS-mediated conversion of the Bu_3SnF into Bu_3SnH. Indeed, this proved to be the case. As indicated in Scheme 2 (conditions B[7]), the catalytic TBAF/PMHS/Bu_3SnF combination gave the desired hydrostannylation products in good yields and with no $Bu_3SnSnBu_3$ formation.[17]

Having applied the Bu_3SnX/PMHS/F^- method of generating Bu_3SnH to in situ hydrostannylations via palladium catalysis, we next decided to investigate the performance of the method in free radical hydrostannylations. We believed the most significant difference between the palladium-mediated and free radical reactions would be the elevated temperatures under which the free radical hydrostannylations are usually conducted. Specifically, we were concerned that in refluxing benzene or toluene our fluoride source would react with the product stannanes, diminishing the overall yield and/or effectively quenching the reaction prematurely.[18]

These concerns proved to be unfounded. As illustrated in Scheme 4,[7] both the catalytic TBAF/PMHS/Bu_3SnF method and the KF/PMHS/Bu_3SnCl performed quite well under free radical reactions. Again the chemical yields and regioselectivities[19] observed in these reactions paralleled those found with the use of commercial tributyltin hydride. Unlike the palladium-catalyzed reactions, the employment of KF/PMHS/Bu_3SnCl under the free radical conditions did not require the inclusion of catalytic TBAF or TBAI. Presumably, the elevated temperatures of the free radical process allow the initial reaction between the KF, Bu_3SnCl, and the PMHS to take place at the water/benzene (or toluene) interface. The free radical reactions were similar to the palladium protocols in many regards, including the compatibility of silyl ethers with the procedure.

Scheme 5



At this point, we needed to address a PMHS-related phenomena, which occasionally complicates the workup of these reactions. Our standard workup usually involves a NaOH treatment, evaporation, and chromatographic purification. With base-sensitive substrates such as the acetate in Scheme 4, the caustic workup needs to be omitted to avoid partial saponification of the ester. In such cases, the NaOH wash can be eliminated from the workup, but when omitted an almost "plastic" substance will occasionally solidify upon evaporation of the reaction solvent. This material is quite insoluble, and significant amounts of the product are usually trapped within the polymer. To avoid this periodic annoyance, we sought a low cost PMHS substitute that could be easily removed from the reaction mixture in an efficient and simple way. Surface-immobilized silyl hydrides on silica such as those popularized by Fry et al.[20] were viewed as excellent candidates for such a PMHS substitute. Reducing silica or "Red-Sil" is relatively simple to make[20a] and when applied to palladium-mediated reductions[20b] can be easily removed by filtration of the reaction mixture. In our reactions,[7] Red-Sil performed admirably (Scheme 5), although a 4-fold excess of silane was required. Importantly, the reactions are very clean, and simple filtration of the reaction mixture through a short pad of silica gel completely removed the silane, which did not contain any detectable amounts of vinylstannane, and simultaneously removed the other reaction salts. Again, no $Bu_3SnSnBu_3$ byproduct was observed.

We have also investigated the application of our new method to the in situ generation and reaction of other tin hydrides, especially trimethyltin hydride. The very high toxicity of trimethyltin hydride coupled with its volatility (59 °C at 760 mmHg)[21] makes this reagent quite dangerous to handle. Ideally, this reagent is best prepared in situ, allowing its use without isolation. However,

(17) Interestingly, the addition of aqueous KF to THF or Et_2O mixtures of Bu_3SnF and PMHS results in the formation of only trace amounts of stannane.

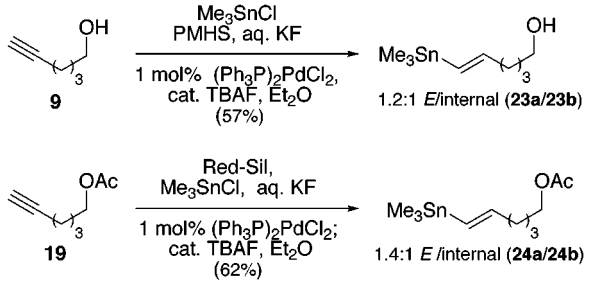
(18) (a) Corey, E. J.; Guzman-Perez, A.; Lazerwith, S. E. *J. Am. Chem. Soc.* **1997**, *119*, 11769−11776. (b) Pearlman, B. A.; Putt, S. R.; Fleming, J. A. *J. Org. Chem.* **1985**, *50*, 3622−3624. (c) Harpp, D. N.; Gingras, M. *J. Am. Chem. Soc.* **1988**, *110*, 7737−7745. (d) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985**, *41*, 4079−4094.

(19) This trend continues when the Bu_3SnCl/KF/PMHS method is used under free radical conditions that promote kinetic *Z*-olefin formation (excess alkyne, short reaction times; Leusink, A. J.; Budding, H. A. *J. Organomet. Chem.* **1968**, *11*, 533−539; Tolstikov, G. A.; Miftakhov, M. S.; Danilova, N. A.; Vel'der, Y. L. *Synthesis* **1986**, 496−499; and ref 3b). However, for reasons that remain unclear, the reactions were significantly less selective for the cis vinylstannanes with the Bu_3SnF/TBAF/PMHS protocol.

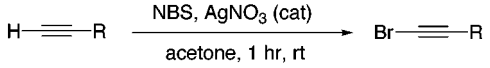
(20) (a) Reed-Mundell, J. J.; Nadkarni, D. V.; Kunz, J. M., Jr.; Fry, C. W.; Fry, J. L. *Chem. Mater.* **1995**, *7*, 1655−1660. (b) Kini, A. D.; Nadkarni, D. V.; Fry, J. L. *Tetrahedron Lett.* **1994**, *35*, 1507−1510. (c) For other immobilized hydrosilanes, see: Rudzinski, W. E.; Montgomery, T. L.; Frye, J. S.; Hawkins, B. L.; Maciel, G. E. *J. Catal.* **1986**, *98*, 444−456.

(21) (a) Scott, W. J.; Moretto, A. F. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. Ed.; Wiley: New York, 1995; Vol. 7, 5327−5328. (b) Dyer, R. S.; Walsh, T. J.; Wonderlin, W. F.; Bercegeay, M. *Neurobehav. Toxicol. Teratol.* **1982**, *4*, 127−133.

Scheme 6



Scheme 7



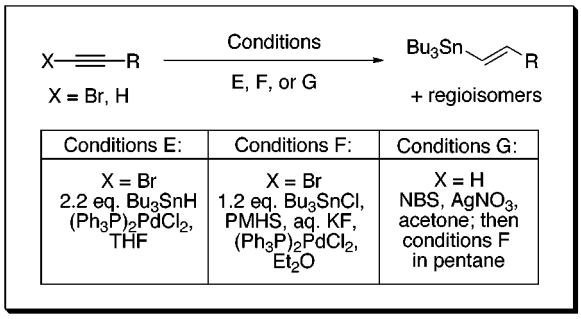
R = —$(CH_2)_4$OH (**9**) (95%) R = —$(CH_2)_4$OH (**25**)
R = —$(CH_2)_4CH_3$ (**21**) (95%) R = —$(CH_2)_4CH_3$ (**26**)
R = —$(CH_2)_3$OTHP (**27**) (97%) R = —$(CH_2)_3$OTHP (**28**)

because of the absence of any commercially available trimethyltin oxides, the synthesis of trimethyltin hydride has traditionally relied on the reaction of strong hydride donors with trimethyltin chloride.[21a] Given the substrate tolerance exhibited by our method, we believed the Me_3SnCl/siloxane/fluoride combination would represent the best way to perform reactions with trimethyltin hydride.[22] Indeed, trimethylvinylstannanes were efficiently prepared via palladium-mediated hydrostannylations[7] with trimethyltin hydride generated from the reaction of Me_3SnCl, $KF_{(aq)}$ and either PMHS or Red-Sil (Scheme 6).

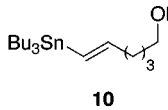
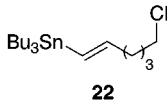
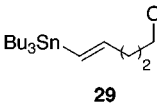
Finally, Guibé[6c] and Pattenden[23] have shown that through the employment of 1-bromo alkynes instead of unsubstituted 1-alkynes the regioselectivity of palladium-mediated hydrostannylations can be improved in favor of the *trans*-vinylstannanes. This transformation typically requires 2 equiv of tin hydride, one for incorporation into the product and the second to effect the reduction of the intermediate vinylbromide, forming 1 equiv of Bu_3SnBr in the process. We decided to investigate if our KF/PMHS methodology could be used to recycle the tin bromide byproduct, thus requiring only 1 equiv of tin for the reaction to go to completion.

Following the general procedure of Pattenden[23] we prepared several 1-bromo alkynes[7] (Scheme 7). These compounds were then subjected to our palladium-catalyzed hydrostannylation conditions, but with only 1.2 equiv of Bu_3SnCl. We were pleased to find that our method for in situ tin hydride generation did allow these reactions to be performed with substoichiometric quantities of tributyltin hydride. As Scheme 8 shows, the yields and isomeric ratios using the KF method proved even higher than those obtained in control experiments[24] using 2.2 equiv of Bu_3SnH (perhaps a benefit of the low tin hydride concentration during the reaction[6c]). We were also able to further simplify this transformation by forming and reacting the 1-bromoalkyne without isolation. This one-pot protocol proceeded with little loss of stereocontrol but with a modest reduction in yields as compared to the stepwise procedure.

Scheme 8



Conditions E:	Conditions F:	Conditions G:
X = Br 2.2 eq. Bu_3SnH $(Ph_3P)_2PdCl_2$, THF	X = Br 1.2 eq. Bu_3SnCl, PMHS, aq. KF, $(Ph_3P)_2PdCl_2$, Et_2O	X = H NBS, $AgNO_3$, acetone; then conditions F in pentane

product	yields Conditions E	Conditions F	Conditions G
 **10**	54% (**10a-c**) *E*/internal/*Z* 11:1:1	51% (**10a-c**) *E*/internal/*Z* 18:1:1	42% (**10a-c**) *E*/internal/*Z* 33:0:1
 **22**	50% (**22a-c**) *E*/internal/*Z* 8:1:1	74% (**22a-c**) *E*/internal/*Z* 18:1:1	48% (**22a-c**) *E*/internal/*Z* 20:0:1
 **29**	69% (**29a-c**) *E*/internal/*Z* 8:1:1	63% (**29a-c**) *E*/internal/*Z* 17:2:1	45% (**29a-c**) *E*/internal/*Z* 17:0:1

Conclusion

In summary, either Bu_3SnCl/PMHS/$KF_{(aq)}$ or the combination of tributyltin fluoride, PMHS, and catalytic quantities of tetrabutylammonium fluoride (TBAF) can serve as in situ sources of tributyltin hydride for both free radical and palladium-catalyzed hydrostannylation reactions. Furthermore, other trialkyltin halides such as trimethyltin chloride, as well as alternative reductants such as Red-Sil appear to be amenable to the method.

Experimental Section

Materials and Methods. Reactions were carried out in oven- or flame-dried glassware under nitrogen atmosphere unless otherwise noted. All commercial reagents were used without purification. All solvents were reagent grade. Diethyl ether and THF were freshly distilled from sodium/benzophenone under nitrogen. Benzene and toluene were freshly distilled from calcium hydride under nitrogen. Except as otherwise indicated, all reactions were magnetically stirred and monitored by thin-layer chromatography with 0.25-mm precoated silica gel plates or capillary GC with a fused silica column. Flash chromatography was performed with silica gel 60 Å (particle size 230−400 mesh ASTM). Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. High-resolution mass spectra (resolution 7000) were obtained at either the Michigan State University Mass Spectrometry Service Center or at the Mass Spectrometry Laboratory of the University of South Carolina, Department of Chemistry & Biochemistry. GC/MS were performed with a fused silica column (30 m by 0.25 mm i.d.).

(22) At 9−20 mg/kg the LD_{50} of Me_3SnCl[3b] is similar to that of Me_3SnH (7 mg/kg in large rats).[21b] However, as a solid (mp 37−38 °C) the Me_3SnCl does not pose the same inhalation hazard as Me_3SnH. Furthermore, the reaction of R_3SnCl with KF/PMHS initially involves the conversion of the tin chlorides into the corresponding tin fluorides,[1] which given their associated nature are generally only sparingly soluble in organic solvents.[3a] Thus, tin poisoning through absorption is also minimized by this protocol.

(23) Boden, C. D. J.; Pattenden, G.; Ye, T. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2417−2419.

(24) In our hands, the control experiments gave somewhat lower levels of regio- and stereocontrol than have been reported in the literature (refs 6c and 23). We are not alone in this experience (see: Blaskovich, M. A.; Kahn, M. *J. Org. Chem.* **1998**, *63*, 1119−1125).

Representative Procedure for Palladium-Mediated Hydrostannylations via Bu_3SnCl, aqueous KF, catalytic TBAF (or TBAI), and Polymethylhydrosiloxane (PMHS). Preparation of 3,5-Dimethyl-1-(tributylstannyl)-1(*E*)-buten-3-ol (4a) and 3,5-Dimethyl-2-(tributylstannyl)-1-buten-3-ol (4b) (Conditions A, Scheme 2). PMHS (0.12 mL, 2.0 mmol) was added to a solution of 3,5-dimethyl-1-hexyn-3-ol (126 mg, 1.0 mmol) (**1**), Bu_3SnCl (0.27 mL, 1.0 mmol), aqueous KF (116 mg, 2.0 mmol; 1 mL H_2O), $(PPh_3)_2PdCl_2$ (7 mg, 0.01 mmol), and tetrabutylammonium iodide (TBAI) crystals (catalytic) in diethyl ether (3 mL). The biphasic reaction mixture was stirred at rt until TLC showed complete consumption of the alkyne (~1 h), at which time 0.5 M NaOH (1 mL) was added and the reaction was allowed to stir an additional 2 h. The two phases were then separated, and the aqueous phase was extracted with diethyl ether (3×). The combined organics were washed with brine and dried over $MgSO_4$. After filtration, the solvent was evaporated, and the residue was purified by flash silica gel chromatography (petroleum ether/EtOAc [95:5]) to afford 263 mg (63%) of 3,5-dimethyl-1-(tributylstannyl)-1(*E*)-buten-3-ol (**4a**) and 11 mg (3%) of 3,5-dimethyl-2-(tributylstannyl)-1-buten-3-ol (**4b**) as clear oils.

For **4a**: IR ($CHCl_3$) 3594, 3463 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.86−0.95 (m, 21 H), 1.22−1.37 (m, 9 H), 1.42−1.55 (m, 8 H), 1.60−1.72 (m, 1 H), 6.01 (d, J = 19.3 Hz, 1 H), 6.08 (d, J = 19.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 122.5, 75.1, 50.8, 29.1, 28.9, 27.3, 24.6, 25.5, 24.4, 13.7, 9.4; GC/MS (EI) m/z 361 (100) [M^+ − Bu]; HRMS (EI) m/z 361.1576 [(M^+ − Bu); calcd for $C_{16}H_{33}OSn$ 361.1556].

For **4b**: IR ($CHCl_3$) 3594 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.84−0.99 (m, 21 H), 1.20−1.37 (m, 9 H), 1.42−1.55 (m, 8 H), 1.62−1.70 (m, 1 H), 5.16 (d, J = 1.4 Hz, 1 H), 5.66 (d, J = 1.7 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 121.1. 78.4, 51.0, 29.8, 29.1, 27.5, 24.8, 24.7, 24.3, 13.7, 10.7; GC/MS (EI) m/z 343 (83) [M^+ − Bu − H_2O], 251 (100); HRMS (EI) m/z 343.1435 [(M^+ − H_2O); calcd for $C_{16}H_{31}Sn$ 343.1448].

3,3-Dimethyl-1-(tributylstannyl)-1(*E*)-butene (6) (Conditions A, Scheme 2). Applying conditions A, 3,3-dimethyl-1-butyne (**5**) (82.2 mg, 1 mmol) afforded after 2 h reaction time and flash silica gel chromatography (hexanes) 220 mg (59%) of 3,3-dimethyl-1-(tributylstannyl)-1(*E*)-butene (**6**) as a clear oil. See Supporting Information for product characterization data.

3-Phenyl-1-(tributylstannyl)-1(*E*)-buten-3-ol (8a) and 3-Phenyl-2-(tributylstannyl)-1-buten-3-ol (8b) (Conditions A, Scheme 2). Conditions A were applied to 2-phenyl-3-butyn-2-ol (**7**) (146 mg, 1.0 mmol) but modified to exclude the NaOH wash.[25] After 1 h reaction time and silica gel chromatography (petroleum ether/EtOAc [95:5]), the reaction afforded 345 mg (79%) of 3-phenyl-1-(tributylstannyl)-1(*E*)-buten-3-ol (**8a**) and 30 mg (7%) of 3-phenyl-2-(tributylstannyl)-1-buten-3-ol (**8b**) as clear oils. See Supporting Information for product characterization data.

1-(Tributylstannyl)-1(*E*)-hexen-6-ol (10a) and 2-(Tributylstannyl)-1-hexen-6-ol (10b) (Conditions A, Scheme 2). Applying conditions A to 5-hexyn-1-ol (**9**) (98 mg, 0.11 mL, 1.0 mmol) afforded after 24 h reaction time and silica gel chromatography (hexane/EtOAc [90:10] with 1% Et_3N) 280 mg (72%) of a mixture (1.4:1) of 1-(tributylstannyl)-1(*E*)-hexen-6-ol (**10a**) and 2-(tributylstannyl)-1-hexen-6-ol (**10b**) as a clear oil. The spectroscopic data for **10a**[7b] and **10b**[7c] were consistent with those previously reported in the literature.

5-(*tert*-Butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-pentene (12a) and 5-(*tert*-Butyldimethylsilyloxy)-2-(tributylstannyl)-1-pentene (12b) (Conditions A, Scheme 2). Applying conditions A to 5-(*tert*-butyldimethylsilyloxy)-1-pentyne (**11**)[7a] (200 mg, 1.01 mmol) afforded after 4 h reaction time and silica gel chromatography (pentane with 1% Et_3N) 260 mg (51%) of a clear oil containing a mixture (1:1) of 5-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-pentene (**12a**) and 5-(*tert*-butyldimethylsilyloxy)-2-(tributylstannyl)-1-pentene (**12b**). See Supporting Information for product characterization data.

5-Chloro-1-(tributylstannyl)-1(*E*)-pentene (16a) and 5-Chloro-2-(tributylstannyl)-1-pentene (16b) (Conditions A, Scheme 2). Applying conditions A to 5-chloro-1-pentyne (**15**) (1.16 mL, 1.0 mmol) afforded after 1 h reaction time and silica gel chromatography (hexanes) 330 mg (84%) of a clear oil containing a mixture (1.4:1) of 5-chloro-1-(tributylstannyl)-1(*E*)-pentene (**16a**) and 5-chloro-2-(tributylstannyl)-1-pentene (**16b**). See Supporting Information for product characterization data.

1-(2(*E*)-Tributylstannylethenyl)-1-cyclohexanol (18a) and 1-(1-Tributylstannylethenyl)-1-cyclohexanol (18b) (Conditions A, Scheme 2). Applying conditions A to 1-ethynyl-1-cyclohexanol (**17**) (124 mg, 1.0 mmol) afforded after 1 h reaction time and silica gel chromatography (hexane/EtOAc [90:10] with 1% Et_3N) 257 mg (62%) of a clear oil containing a mixture (17:1) of 1-(2(*E*)-tributylstannylethenyl)-1-cyclohexanol (**18a**) and 1-(1-tributylstannylethenyl)-1-cyclohexanol (**18b**). The spectroscopic data for **18a** were consistent with those previously reported in the literature.[26] See Supporting Information for product characterization data on **18b**.

1-(Trimethylstannyl)-1(*E*)-hexen-6-ol (23a) and 2-(Trimethylstannyl)-1-hexen-6-ol (23b) (Conditions A, with Me_3SnCl, Scheme 6). Applying conditions A to 5-hexyn-1-ol (**9**) (98 mg, 0.12 mL, 1.0 mmol) and Me_3SnCl (0.20 g, 1.0 mmol) afforded after 3 h reaction time and silica gel chromatography (hexane/EtOAc [90:10] with 1% Et_3N) 150 mg (57%) of a clear oil containing a mixture (1.2:1) of 1-(trimethylstannyl)-1(*E*)-hexen-6-ol (**23a**) and 2-(trimethylstannyl)-1-hexen-6-ol (**23b**). See Supporting Information for product characterization data.

6-Aceto-1-(trimethylstannyl)-1(*E*)-hexene (24a) and 6-Aceto-2-(trimethylstannyl)-1-hexene (24b) (Conditions A, with Me_3SnCl and Red-Sil, Scheme 6). A solution of the 6-aceto-1-hexyne (**19**)[7c] (0.16 g, 1.14 mmol), Me_3SnCl (200 mg, 1.0 mmol), Red-Sil (1.5 g, 3.15 mmol; 2.1 mmol/g), aqueous KF (58 mg, 1.0 mmol; 0.1 mL H_2O), TBAF crystals (catalytic), and $(PPh_3)_2PdCl_2$ (7 mg, 0.01 mmol) in diethyl ether (5 mL) was stirred at room temperature. After 3 h the reaction mixture was filtered through a pad of Celite and $MgSO_4$. The filter cake containing the Red-Sil was washed with ether several times before the solvent was concentrated. The residue was purified by flash silica gel chromatography (hexanes/EtOAc [95:5] with 1% Et_3N) to afford 0.19 g (62%) of a clear oil containing a mixture (1.4:1) of 6-aceto-1-(trimethylstannyl)-1(*E*)-hexene (**24a**) and 6-aceto-2-(trimethylstannyl)-1-hexene (**24b**). IR (neat) 1741 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) for **24a** δ 0.11 (s, 9 H), 1.43 (m, 2 H), 1.60 (m, 2 H), 2.02 (s, 3 H), 2.13 (m, 2 H), 4.04 (t, J = 6.6 Hz, 2 H), 5.93 (m, 2 H), for **24b** δ 0.08 (s, 9 H), 1.43 (m, 2 H), 1.60 (m, 2 H), 2.02 (s, 3 H), 2.28 (tt, J = 7.4, 1.1 Hz, 2 H), 4.04 (t, J = 6.6 Hz, 2 H), 5.12 (dt, J = 12.8, 1.1 Hz, 1 H), 5.62 (dt, J = 12.8, 1.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) for **24a** δ 171.2, 148.7, 128.5, 62.8, 37.2, 32.2, 24.8, −9.8, for **24b** δ 171.2, 155.2, 124.9, 64.3, 40.2, 28.1, 25.7, 21.0, −9.5; HRMS (CI) m/z 307.0721 [(M^+); calcd for $C_{11}H_{22}O_2Sn$, 307.0722].

Representative Procedure for the Palladium-Mediated Hydrostannylations via Bu_3SnF, catalytic TBAF, and PMHS. Preparation of 6-(*tert*-Butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-hexene (14a) and 6-(*tert*-Butyldimethylsilyloxy)-2-(tributylstannyl)-1-hexene (14b) (Conditions B, Scheme 2). A solution of 6-(*tert*-butyldimethylsilyloxy)-1-hexyne (430 mg, 2.02 mmol) (**13**),[7b] Bu_3SnF (0.65 g, 2.1 mmol), PMHS (0.13 mL, 2.1 mmol), TBAF crystals (catalytic), and $(PPh_3)_2PdCl_2$ (14 mg, 0.02 mmol) in diethyl ether (20 mL) was stirred at rt for 2.5 h, at which time 0.5 M NaOH (2 mL) was added and the reaction was allowed to stir an additional 2 h. The reaction mixture was then filtered, and

(25) For reasons that remain unclear, working up the palladium-catalyzed hydrostannylations of 2-phenyl-3-butyn-2-ol (**7**) with NaOH resulted in the intrusive formation (12%) of the homocoupled diene (Alcaraz, L.; Taylor, R. J. K. *Synlett* **1997**, 791−792 and references therein).

(26) Betzer, J.-F.; Delaloge, F.; Muller, B.; Pancrazi, A.; Prunet, J. *J. Org. Chem.* **1997**, *62*, 7768−7780.

the filtrate was washed with brine. The aqueous layer was back extracted with ether (2×), and the combined organics were dried over $MgSO_4$ and concentrated. The residue was purified by flash silica gel chromatography (pentane with 1% Et_3N) to afford 300 mg (30%) of 6-(*tert*-butyldimethylsilyloxy)-1(*E*)-(tributylstannyl)-1-hexene (**14a**) and 230 mg (23%) of 6-(*tert*-butyldimethyl-silyloxy)-2-(tributylstannyl)-1-hexene (**14b**) as clear oils.

For **14a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 6 H), 0.85 (m, 18 H), 1.20−1.40 (m, 8 H), 1.40−1.60 (m, 14 H), 2.12 (m, 2 H), 3.59 (t, J = 6.6 Hz, 2 H), 5.80−6.04 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 127.3, 63.2, 37.6, 32.3, 29.1 (2C), 27.3, 26.0, 18.4, 13.7, 9.4, −5.3; HRMS (CI) *m*/*z* 503.2755 [(M^+); calcd for $C_{24}H_{52}OSiSn$ 503.2735].

For **14b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 6 H), 0.85 (m, 18 H), 1.20−1.40 (m, 8 H), 1.40−1.60 (m, 14 H), 2.23 (t, J = 7.4 Hz, 2 H), 3.59 (t, J = 6.6 Hz, 2 H), 5.07 (dt, J = 3.0, 1.1 Hz, 1 H), 5.64 (dt, J = 3.0, 1.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5, 124.7, 63.1, 41.2, 32.5, 29.1 (2C), 27.4, 26.0, 18.4, 13.7, 9.5, −5.3; HRMS (CI) *m*/*z* 503.2755 [(M^+); calcd for $C_{24}H_{52}OSiSn$ 503.2735].

3,5-Dimethyl-1-(tributylstannyl)-1(*E*)-buten-3-ol (4a) and 3,5-Dimethyl-2-(tributylstannyl)-1-buten-3-ol (4b) (Conditions B, Scheme 2). Applying conditions B to 3,5-dimethyl-1-hexyn-3-ol (**1**) (0.07 mL, 0.5 mmol) afforded after 1 h reaction time and silica gel chromatography (petroleum ether/EtOAc [95:5]) 134 mg (64%) of 3,5-dimethyl-1-(tributylstannyl)-1(*E*)-buten-3-ol (**4a**) and 6 mg (3%) of 3,5-dimethyl-2-(tributylstannyl)-1-buten-3-ol (**4b**) as clear oils. See Supporting Information for product characterization data.

3,3-Dimethyl-1-(tributylstannyl)-1(*E*)-butene (6) (Conditions B, Scheme 2). Applying conditions B to 3,3-dimethyl-1-butyne (411 mg, 5.0 mmol) (**5**) afforded after 2 h and silica gel chromatography (petroleum ether) 1.25 g (67%) of 3,3-dimethyl-1-(tributylstannyl)-1(*E*)-butene (**6**) as a clear oil. See Supporting Information for product characterization data.

3-Phenyl-1-(tributylstannyl)-1(*E*)-buten-3-ol (8a) (Conditions B, Scheme 2). Conditions B were applied to 2-phenyl-3-butyn-2-ol (**7**) (146 mg, 1.0 mmol) but modified to exclude the NaOH wash.[25] Thus, after 1.5 h reaction time, the reaction was diluted with hexanes (15 mL) and washed with water and then brine. The organics were dried over $MgSO_4$, concentrated, and purified by silica gel chromatography (hexanes/EtOAc [90:10] with 1% Et_3N) to afford 300 mg (68%) of 3-phenyl-1-(tributylstannyl)-1(*E*)-buten-3-ol (**8a**) as a clear oil. See Supporting Information for product characterization data.

1-(Tributylstannyl)-1(*E*)-hexen-6-ol (10a) and 2-(Tributylstannyl)-1-hexen-6-ol (10b) (Conditions B, Scheme 2). Applying conditions B to 5-hexyn-1-ol (**9**) (98 mg, 0.11 mL, 1.0 mmol) afforded after 2 h reaction time and silica gel chromatography (hexane/EtOAc [90:10] with 1% Et_3N) 160 mg (41%) of 1-(tributylstannyl)-1(*E*)-hexen-6-ol (**10a**), 111 mg (28%) as a mixture(1:1.3) of **10a** and **10b**, and 30 mg (8%) of 2-(tributylstannyl)-1-hexen-6-ol (**10b**) as clear oils. See Supporting Information for product characterization data.

5-Chloro-1-(tributylstannyl)-1(*E*)-pentene (16a) and 5-Chloro-2-(tributylstannyl)-1-pentene (16b) (Conditions B, Scheme 2). Applying conditions B to 5-chloro-1-pentyne (**15**) (1.07 mL, 1.0 mmol) afforded after 0.5 h reaction time and silica gel chromatography (hexanes) 310 mg (78%) of a clear oil containing a mixture (1.4:1) of 5-chloro-1-(tributylstannyl)-1(*E*)-pentene (**16a**) and 5-chloro-2-(tributylstannyl)-1-pentene (**16b**). See Supporting Information for product characterization data.

1-(2(*E*)-Tributylstannylethenyl)-1-cyclohexanol (18a) (Conditions B, Scheme 2). Applying conditions B to 1-ethynyl-1-cyclohexanol (124 mg, 1.0 mmol) (**17**) afforded after 3.5 h time and silica gel chromatography (hexane/EtOAc [90:10] with 1% Et_3N) 290 mg (70%) of 1-(2(*E*)-tributylstannylethenyl)-1-cyclohexanol (**18a**)[26] as a clear oil.

1-(2(*E*)-Tributylstannylethenyl)-1-cyclohexanol (18a) and 1-(1-Tributylstannylethenyl)-1-cyclohexanol (18b) (Conditions B, with Red-Sil, Scheme 5). A solution of 1-ethynyl-1-cyclohexanol (27 mg, 0.22 mmol) (**17**), Bu_3SnF (68 mg, 0.22 mmol), Red-Sil (110 mg, 0.23 mmol; 2.1 mmol/g), TBAF crystals (catalytic), and $(PPh_3)_2PdCl_2$ (2 mg, 0.003 mmol) in diethyl ether (5 mL) was stirred at room temperature. At 50 min intervals, two additional portions of Red-Sil were added (total of 330 mg, 0.69 mmol). After 2.5 h, the reaction mixture was filtered through a pad of silica gel and the solvent was evaporated to yield 70 mg (76%) of a light yellow oil containing a mixture (19:1) of 1-(2(*E*)-tributylstannylethenyl)-1-cyclohexanol (**18a**) and 1-(1-tributylstannylethenyl)-1-cyclohexanol (**18b**). These isomers could be separated by flash silica gel chromatography (petroleum ether/EtOAc [95:5]). See Supporting Information for product characterization data.

Representative Procedure for the Free Radical Hydrostannylations via Bu_3SnCl, aqueous KF, catalytic TBAF (or TBAI), and PMHS. Preparation of 6-(*tert*-Butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-hexene (14a) and 6-(*tert*-Butyldimethylsilyloxy)-1-(tributylstannyl)-1(*Z*)-hexene (14c) (Conditions C, Scheme 4). A round-bottom flask containing a solution of 6-(*tert*-butyldimethylsilyloxy)-1-hexyne (**13**)[7b] (430 mg, 2.02 mmol), Bu_3SnCl (0.65 mL, 2.4 mmol), aqueous KF (350 mg, 6.02 mmol; 0.5 mL H_2O), PMHS (0.14 mL, 2.4 mmol), and AIBN (16 mg, 0.1 mmol) in toluene (10 mL) was immersed in a preheated (∼75 °C) oil bath. After stirring for 2 h at this temperature, the reaction mixture was cooled, and 0.5 M NaOH (2 mL) was added. Stirring continued for 2 h, at which time the reaction was filtered. The filtrate layers were separated, and the aqueous phase was back extracted with ether. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated. The crude material was then purified by flash silica gel chromatography (pentane with 1% Et_3N) to afford 610 mg (60%) of a clear oil containing a mixture (4:1) of 6-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-hexene (**14a**) and 6-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*Z*)-hexene (**14c**). For spectroscopic data on **14a** see above. For **14c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 6 H), 0.85 (m, 18 H), 1.20−1.40 (m, 8 H), 1.40−1.60 (m, 14 H), 2.02 (m, 2 H), 3.59 (t, J = 6.6 Hz, 2 H), 5.77 (dt, J = 12.4, 1.1 Hz, 1 H), 6.48 (dt, J = 12.4, 6.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 127.9, 63.2, 36.9, 32.7, 29.1 (2C), 27.3, 25.1, 18.4, 13.7, 10.2, −5.3.

1-(Tributylstannyl)-1(*E*)-hexen-6-ol (10a) and 1-(Tributylstannyl)-1(*Z*)-hexen-6-ol (10c) (Conditions C, Scheme 4). Applying conditions C to 5-hexyn-1-ol (**9**) (294 mg, 0.33 mL, 3.0 mmol) afforded after silica gel chromatography (hexane/EtOAc [90:10] with 1% Et_3N) 724 mg (62%) of a clear oil containing a mixture (3.3:1) of 1-(tributylstannyl)-1(*E*)-hexen-5-ol (**10a**) and 1-(tributylstannyl)-1(*Z*)-hexen-5-ol (**10c**). See Supporting Information for product characterization data.

1-(2(*E*)-Tributylstannylethenyl)-1-cyclohexanol (18a), 1-(1-Tributylstannylethenyl)-1-cyclohexanol (18b), and 1-(2(*Z*)-Tributylstannylethenyl)-1-cyclohexanol (18c). (Conditions C, Scheme 4). Applying conditions C to 1-ethynyl-1-cyclohexanol (**17**) (248 mg, 2.0 mmol) afforded after silica gel chromatography (hexane/EtOAc [90:10] with 1% Et_3N) 0.40 g (48%) of 1(*E*)-(2-tributylstannylethenyl)-1-cyclohexanol (**18a**) as a clear oil (see above for spectroscopic data) along with 27 mg (3%) of a clear oil containing a mixture (5:1) of 1-(1-tributylstannylethenyl)-1-cyclohexanol (**18b**) and 1-(2(*Z*)-tributylstannylethenyl)-1-cyclohexanol (**18c**). See Supporting Information for product characterization data.

6-Aceto-1-(tributylstannyl)-1(*E*)-hexene (20a) and 6-Aceto-1-(tributylstannyl)-1(*Z*)-hexene (20c) (Conditions C, Scheme 4). Conditions C were applied to 6-aceto-1-hexyne (**19**)[7c] (140 mg, 1.0 mmol) but modified to exclude the NaOH wash. Thus, after 3 h reaction time, the reaction mixture was cooled and filtered. The filtrate was concentrated, and the crude material was then purified by silica gel chromatography (hexanes/EtOAc [97:3] with 1% Et_3N) to afford 240 mg (56%) of a clear oil containing a mixture (3.9:1) of 6-aceto-1-(tributylstannyl)-1(*E*)-hexene (**20a**) and 6-aceto-1-(tributylstannyl)-1(*Z*)-hexene (**20c**). See Supporting Information for product characterization data.

1-(Tributylstannyl)-1(*E*)-heptene (22a) and 1-(Tributylstannyl)-1(*Z*)-heptene (22c) (Conditions C, Scheme 4). Applying conditions C to 1-heptyne (**21**) (192 mg, 0.26 mL, 2.0 mmol) afforded after silica gel chromatography (hexanes) 390

mg (50%) of a clear oil containing a mixture (4:1) of 1-(tributylstannyl)-1(*E*)-heptene (**22a**) and 1-(tributylstannyl)-1(*Z*)-heptene (**22c**). The spectroscopic data for **22a** and **22c** were consistent with those previously reported in the literature.[27]

Representative Procedure for the Free Radical Hydrostannylations via Bu_3SnF, catalytic TBAF, and PMHS. Preparation of 1-(Tributylstannyl)-1(*E*)-hexen-6-ol (10a) and 1-(Tributylstannyl)-1(*Z*)-hexen-6-ol (10c) (Conditions D, Scheme 4). A round-bottom flask containing a solution of 5-hexyne-1-ol (294 mg, 0.33 mL 3.0 mmol) (**9**), Bu_3SnF (1.12 g, 3.6 mmol), TBAF crystals (catalytic), PMHS (0.22 mL, 3.6 mmol), and AIBN (25 mg, 0.15 mmol) in benzene (20 mL) was immersed in a preheated (~75 °C) oil bath. After stirring for 2 h at this temperature, the reaction mixture was cooled, and 0.5 M NaOH (2 mL) was added. Stirring continued for 2 h, at which time diethyl ether (20 mL) was added, and the layers were separated. The organic phase was washed with water and brine and then dried over $MgSO_4$. The mixture was filtered and concentrated, and the crude material was then purified by flash silica gel chromatography (hexane/EtOAc [95:5]) to afford 1.07 g (91%) of a clear oil containing a mixture (3.1:1) of 1-(tributylstannyl)-1(*E*)-hexen-6-ol (**10a**) and 1-(tributylstannyl)-1(*Z*)-hexen-6-ol (**10c**). See Supporting Information for product characterization data.

6-(*tert*-Butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-hexene (14a) and 6-(*tert*-Butyldimethylsilyloxy)-1-(tributylstannyl)-1(*Z*)-hexene (14c) (Conditions D, Scheme 4). Applying conditions D to 6-(*tert*-butyldimethylsilyloxy)-1-hexyne (**13**)[7b] (430 mg, 2.02 mmol) afforded after silica gel chromatography (pentane with 1% Et_3N) 510 mg (51%) of a clear oil containing a mixture (4:1) of 6-(*tert*-butyldimethylsilyloxy)-1-(tributylstannyl)-1(*E*)-hexene (**14a**) and 6-(*tert*-butyldimethyl-silyloxy)-1-(tributylstannyl)-1(*Z*)-hexene (**14c**). See Supporting Information for product characterization data.

1-(2(*E*)-Tributylstannylethenyl)-1-cyclohexanol (18a) and 1-(2(*Z*)-Tributylstannyl-ethenyl)-1-cyclohexanol (18c) (Conditions D, Scheme 4). Applying conditions D to 1-ethynyl-1-cyclohexanol (**17**) (372 mg, 3.0 mmol) afforded after silica gel chromatography (hexane/EtOAc [90:10]) 0.79 g (63%) of a clear oil containing a mixture (77:1) of 1-(2(*E*)-tributylstannylethenyl)-1-cyclohexanol (**18a**) and 1-(2(*Z*)-tributylstannylethenyl)-1-cyclohexanol (**18c**). See Supporting Information for product characterization data.

6-Aceto-1-(tributylstannyl)-1(*E*)-hexene (20a) and 6-Aceto-1-(tributylstannyl)-1(*Z*)-hexene (20c) (Conditions D, Scheme 4). Conditions D were applied to 6-aceto-1-hexyne (**19**) (420 mg, 3 mmol) but modified to exclude the NaOH wash. Thus, after 2 h reaction time, the reaction mixture was cooled and filtered. The filtrate was concentrated, and the crude material was then purified by silica gel chromatography (hexanes/EtOAc [97:3] with 1% Et_3N) to afford 890 mg (69%) of a clear oil containing a mixture (4:1) of 6-aceto-1-(tributylstannyl)-1(*E*)-hexene (**20a**) and 6-aceto-1-(tributylstannyl)-1(*Z*)-hexene (**20c**). See Supporting Information for product characterization data.

1-(Tributylstannyl)-1(*E*)-heptene (22a) and 1-(Tributylstannyl)-1(*Z*)-heptene (22c) (Conditions D, Scheme 4). Applying conditions D to 1-heptyne (**21**) (0.39 mL, 3.0 mmol) afforded after silica gel chromatography (hexanes) 610 mg (53%) of a clear oil containing a mixture (4:1) of 1-(tributylstannyl)-1(*E*)-heptene (**22a**) and 1-(tributylstannyl)-1(*Z*)-heptene (**22c**). See Supporting Information for product characterization data.

Preparation of 1-Bromoalkenes (Scheme 7). 1-Bromo-1-hexyn-6-ol (25). *N*-Bromosuccinimide (NBS) (1.96 g, 11 mmol) and catalytic $AgNO_3$ (150 mg, 0.88 mmol) were added to a solution of 5-hexyn-1-ol (0.98 g, 10 mmol) (**9**) in dry acetone (40 mL). The reaction was stirred at rt until complete by GC (~1 h). At that time, the mixture was diluted with pentane (200 mL) and washed with water (2 × 50 mL). The separated aqueous layer was back extracted with diethyl ether/pentane (1:1, 100 mL), and the combined organics were dried over $MgSO_4$, filtered, and concentrated to afford 1.68 g (95%)1-bromo-1-hexyn-6-ol (**25**),[28] which was used without further purification in the hydrostannylation step (see below). IR (neat) 2363 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.59 (m, 4 H), 2.01 (bs, 1 H), 2.21 (t, J = 6.9 Hz, 2 H), 3.61 (t, J = 6.2 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 79.9, 62.2, 38.0, 31.6, 24.5, 19.4; GC/MS (EI) m/z 176 (1) [$M^+ - H$], 174 (1), 79 (35), 77 (100); HRMS (EI) m/z 175.9837 [(M^+); calcd for C_6H_9BrO 175.9837].

1-Bromo-1-heptyne (26). Following the procedure for the preparation of **25**, 1-heptyne (1.3 mL, 10 mmol) (**21**) was converted into 1.66 g (95%) 1-bromo-1-heptyne (**26**),[29] which was used without further purification in the hydrostannylation step (see below). See Supporting Information for product characterization data.

1-Bromo-5-(tetrahydropyranyloxy)-1-pentyne (28). Following the established procedures,[7d] 1-pentyn-4-ol (0.93 mL, 10 mmol) was converted to 1.59 g of 5-(tetrahydropyranyloxy)-1-pentyne (**27**) (95% yield following flash silica gel chromatography (pentane/EtOAc [95:5]). Then, following the procedure for the preparation of **25**, compound **27** (1.5 g, 8.9 mmol) was converted into 2.13 g (97%) 1-bromo-5-(tetrahydropyranyloxy)-1-pentyne (**28**),[30] which was used without further purification in the hydrostannylation step (see below). See Supporting Information for product characterization data.

Hydrostannylations of 1-bromoalkenes (Scheme 8). Representative Procedure for Hydrostannylations with Commercial Bu_3SnH. Preparation of 1-(Tributylstannyl)-1(*E*)-hexen-6-ol (10a), 2-(Tributylstannyl)-1-hexen-6-ol (10b), and 1-(Tributylstannyl)-1(*Z*)-hexen-6-ol (10c) (Conditions E). Bu_3SnH (0.32 mL, 1.2 mmol) was added dropwise over 30 min to a 0 °C solution of 1-bromo-1-hexyn-6-ol (161 mg, 0.91 mmol) (**25**) and $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) in THF (5 mL). After 2 h, the reaction mixture was concentrated, and diethyl ether (5 mL) and a saturated KF solution (7 mL) were added. This mixture was allowed to stir for 4 h before being filtered. The filtrate layers were separated, and the aqueous layer was extracted with ether. The combined organic phases were then washed with H_2O and brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash silica gel chromatography (pentane/EtOAc [95:5 to 90:10] with 1% Et_3N) to afford 193 mg (54%) of a pale yellow clear oil that contained a mixture (11:1:1) of 1-(tributylstannyl)-1(*E*)-hexen-6-ol (**10a**), 2-(tributylstannyl)-1-hexen-6-ol (**10b**), and 1-(tributylstannyl)-1(*Z*)-hexen-6-ol (**10c**). See Supporting Information for product characterization data.

1-(Tributylstannyl)-1(*E*)-heptene (22a), 2-(Tributylstannyl)-1-heptene (22b), and 1-(Tributylstannyl)-1(*Z*)-heptene (22c) (Conditions E). Applying conditions E to 1-bromo-1-heptyne (175 mg, 1.0 mmol) (**26**) afforded after flash silica gel chromatography (pentane with 1% Et_3N) 194 mg (50%) of a clear yellow oil that contained a mixture (8:1:1) of 1-(tributylstannyl)-1(*E*)-heptene (**22a**), 2-(tributylstannyl)-1-heptene (**22b**), and 1-(tributylstannyl)-1(*Z*)-heptene (**22c**). See Supporting Information for product characterization data.

5-(Tetrahydropyranyloxy)-1(*E*)-(tributylstannyl)-1-pentene (29a), 5-(Tetrahydropyranyloxy)-2-(tributylstannyl)-1-pentene (29b), and 5-(Tetrahydropyranyloxy)-1(*Z*)-(tributylstannyl)-1-pentene (29c) (Conditions E). Applying conditions E to 1-bromo-5-(tetrahydropyranyloxy)-1-pentyne (247 mg, 1 mmol) (**28**) afforded after flash silica gel chromatography (pentane/EtOAc [95:5] with 1% Et_3N) 316 mg (69%) of a cloudy colorless oil that contained a mixture (8:1:1) of 5-(tetrahydropyranyloxy)-1(*E*)-(tributylstannyl)-1-pentene (**29a**), 5-(tetrahydropyranyloxy)-2-(tributylstannyl)-1-pentene (**29b**), and 5-(tetrahydropyranyloxy)-1(*Z*)-(tributylstannyl)-1-pentene (**29c**). The spectroscopic data for **29a**[7d] and **29b**[7c] were consistent with those previously reported in the literature.

(27) Cliff, M. D.; Pyne, S. G. *Tetrahedron* **1996**, *52*, 13703−13712.

(28) For a prior preparation, boiling point, and IR data for **25**, see: Yee, K. C. US Patent 4,125,534, 1978; *Chem. Abst.* **1979**, *90*, 88046.

(29) For a prior preparation of **26**, see: Straus, F.; Kollek, L.; Heyn, W. *Chem. Ber.* **1930**, *63*, 1868−1885.

(30) For a prior preparation of **28** without spectroscopic data, see ref 23.

Representative Procedure for Hydrostannylations with Catalytic Bu_3SnH Generated in Situ from KF/PMHS. Preparation of 1-(Tributylstannyl)-1(*E*)-hexen-6-ol (10a), 2-(Tributylstannyl)-1-hexen-6-ol (10b), and 1-(Tributylstannyl)-1(*Z*)-hexen-6-ol (10c) (Conditions F). PMHS (0.18 mL, 3.0 mmol) was added to a solution of KF (176 mg, 3.0 mmol; 1 mL H_2O), $PdCl_2(PPh_3)_2$ (3.5 mg, 0.005 mmol), Bu_3SnCl (0.32 mL, 1.2 mmol), and TBAI (cat.) and 1-bromo-1-hexyn-6-ol (177 mg, 1 mmol) (**25**) in diethyl ether (5 mL). The biphasic mixture was stirred at rt for 4.5 h, at which time 3 M NaOH (1 mL) was added, and the reaction was allowed to stir an additional 3 h. The reaction mixture was separated, and the aqueous phase was extracted with diethyl ether. The combined organics were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash silica gel chromatography (pentane/EtOAc [95:5 to 90:10] with 1% Et_3N) to afford 200 mg (51%) of a clear colorless oil that contained a mixture (18:1:1) of 1-(tributylstannyl)-1(*E*)-hexen-6-ol (**10a**), 2-(tributylstannyl)-1-hexen-6-ol (**10b**), and 1-(tributylstannyl)-1(*Z*)-hexen-6-ol (**10c**). See Supporting Information for product characterization data.

1-(Tributylstannyl)-1(*E*)-heptene (22a), 2-(Tributylstannyl)-1-heptene (22b), and 1-(Tributylstannyl)-1(*Z*)-heptene (22c) (Conditions F). Conditions F were applied to 1-bromo-1-heptyne (175 mg, 1.0 mmol) (**25**) to afford after flash silica gel chromatography (pentane with 1% Et_3N) 285 mg (74%) of a clear pale yellow oil that contained a mixture-(18:1:1) of 1-(tributylstannyl)-1(*E*)-heptene (**22a**), 2-(tributylstannyl)-1-heptene (**22b**), and 1-(tributylstannyl)-1(*Z*)-heptene (**22c**). See Supporting Information for product characterization data.

5-(Tetrahydropyranyloxy)-1(*E*)-(tributylstannyl)-1-pentene (29a), 5-(Tetrahydropyranyloxy)-2-(tributylstannyl)-1-pentene (29b), and 5-(Tetrahydropyranyloxy)-1(*Z*)-(tributylstannyl)-1-pentene (29c) (Conditions F). Conditions F were applied to 1-bromo-5-(tetrahydropyranyloxy)-1-pentyne (247 mg, 1 mmol) (**28**) to afford after flash silica gel chromatography (95:5 pentane/EtOAc with 1% Et_3N) 289 mg (63%) of a clear oil containing a mixture (17:2:1) of 5-(tetrahydropyranyloxy)-1(*E*)-(tributylstannyl)-1-pentene (**29a**), 5-(tetrahydropyranyloxy)-2-(tributylstannyl)-1-pentene (**29b**), and 5-(tetrahydropyranyloxy)-1(*Z*)-(tributylstannyl)-1-pentene (**29c**). See Supporting Information for product characterization data.

Representative Procedure for the One-Pot Bromination/Hydrostannylation Protocol. Preparation of 1-(Tributylstannyl)-1(*E*)-hexen-6-ol (10a) and 1-(Tributylstannyl)-1(*Z*)-hexen-6-ol (10c) (Conditions G). *N*-Bromosuccinimide (NBS) (0.20 g, 1.1 mmol) and catalytic $AgNO_3$ (5 mg, 0.03 mmol) were added to a solution of 5-hexyn-1-ol (0.11 mL, 0.98 mmol) (**9**) in acetone (4 mL). The reaction was stirred at rt until complete by GC (~1 h). At this time, Bu_3SnCl (0.32 mL, 1.2 mmol), KF (232 mg, 4.0 mmol), TBAI (cat.), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol), PMHS (0.09 mL, 1.5 mmol), pentane (4 mL), and H_2O (1 mL) were added successively. This mixture was allowed to stir for 4.5 h. Then, 3 M NaOH (3 mL) was added, and the mixture was allowed to stir an additional 3 h before being filtered. The filtrate phases were separated, and the aqueous phase was extracted with pentane. The combined organics were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash silica gel chromatography (pentane/EtOAc [95:5 to 90:10] with 1% Et_3N) to afford 163 mg (42%) of a clear pale yellow oil that contained a mixture (33:1) of 1-(tributylstannyl)-1(*E*)-hexen-6-ol (**10a**) and 1-(tributylstannyl)-1(*Z*)-hexen-6-ol (**10c**). See Supporting Information for product characterization data.

1-(Tributylstannyl)-1(*E*)-heptene (22a) and 1-(Tributylstannyl)-1(*Z*)-heptene (22c) (Conditions G). Conditions G were applied to 1-heptyne (0.13 mL, 1.0 mmol) (**21**) to afford after flash silica gel chromatography (pentane with 1% Et_3N) 184 mg (48%) of a clear pale yellow oil that contained a mixture (20:1) of 1-(tributylstannyl)-1(*E*)-heptene (**22a**) and 1-(tributylstannyl)-1(*Z*)-heptene (**22c**). See Supporting Information for product characterization data.

5-(Tetrahydropyranyloxy)-1(*E*)-(tributylstannyl)-1-pentene (29a) and 5-(Tetrahydropyranyloxy)-1(*Z*)-(tributylstannyl)-1-pentene (29c) (Conditions G). Conditions G were applied to 5-(tetrahydropyranyloxy)-1-pentyne (168 mg, 1 mmol) (**27**)[7d] to afford after flash silica gel chromatography (pentane/EtOAc [95:5] with 1% Et_3N) 206 mg (45%) of a cloudy colorless oil that contained a mixture (17:1) of 5-(tetrahydropyranyloxy)-1(*E*)-(tributylstannyl)-1-pentene (**29a**) and 5-(tetrahydropyranyloxy)-1(*Z*)-(tributylstannyl)-1-pentene (**29c**). See Supporting Information for product characterization data.

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Supporting Information Available: Spectroscopic data for all new compounds pictured and detailed experimental procedures. This material is available free of charge via the Internet at http:/pubs.acs.org.

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