Exploring the Reactivity of Alkenes Bearing Silicon and/or Tin in the Hydroxyl-Directed Hydrogenation. A Diastereoselective Synthesis of Heterobimetallic Compounds

Mark Lautens,*[1a] C. H. Zhang, Betty Jane Goh,[1b] Cathleen M. Crudden, and Marc J. A. Johnson[1b]

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

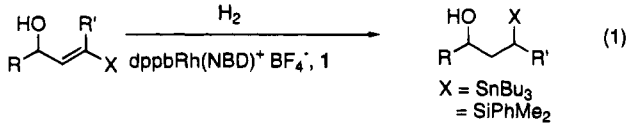
Received May 17, 1994®

The hydroxyl-directed hydrogenation of (*E*)- and (*Z*)-γ-hydroxy vinylstannanes and silanes has been studied in the presence of (dppb)Rh(NBD)BF_4 (**1**). Efficient routes to γ-hydroxy stannanes and silanes have been developed. Diastereoselectivities from 60 to >500:1 were observed. A significant difference in reaction rate and pathway was observed between the (*E*)- and (*Z*)-vinylstannanes. We observed a reductive destannation process for the (*Z*)-stannanes which was influenced by the size of the R group. Competition studies were carried out to determine if steric or electronic effects were responsible for the reactivity patterns observed.

Introduction

Directed reactions are increasingly utilized for the diastereo- and enantioselective construction of complex molecules. The hydroxyl group is particularly efficient for the directed epoxidation, hydrogenation, cyclopropanation, and hydride reduction reactions.[2]

We were interested in exploring the hydroxyl-directed hydrogenation of an olefin bearing a silicon or tin moiety in order to evaluate the feasibility of the reduction as well as the use of the products in organic synthesis. Prior to our studies, vinylstannanes were regarded as unreactive toward typical hydrogenation conditions and little information was available on the reduction of vinylsilanes.[3] We were particularly interested in evaluating the reactivity of alkenes bearing a silicon and tin since there exists considerable interest in novel 1,1-heterobimetallic compounds.[4] In this full account of our studies in this area, we report the highly diastereoselective hydrogenation of olefins bearing silicon and tin substituents catalyzed by cationic rhodium complex **1** and show the scope and limitations of the range of substrates which are successfully hydrogenated, eq 1.[5] We have observed a novel reductive destannation with some substrates and have defined the structural parameters which lead to this process. We also briefly describe competition studies to determine the relative reactivity of vinylsilanes, vinylstannanes, and alkenes bearing both substituents and oxidative reactions of the alkylsilanes and stannanes.



(1)

The directed hydrogenation of an olefin containing an allylic or homoallylic alcohol was first described by Thompson[6] in 1971, but the full potential of this reaction for the control of acyclic stereochemistry was not realized until a series of reports published between 1982 and 1986 by Brown, Stork, Crabtree, and Evans.[7] These studies established the optimum conditions vis-a-vis catalyst, solvent, and hydrogen pressure. Soluble cationic transi-

® Abstract published in *Advance ACS Abstracts,* September 15, 1994.

(1) (a) E. W. R. Steacie Fellow 1994–1996, Alfred P. Sloan Foundation Fellow 1991–1995, NSERC (Canada) University Research Fellow 1987–1997, BioMega Young Investigator 1990–1993, Eli Lilly Grantee 1992–1994. (b) Undergraduate research participants.

(2) For a recent review, see: Evans, D. A.; Hoveyda, A. H.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307. Selected references: Epoxidation: (a) Henbest, H. B.; Wilson, R.A. *J. Chem. Soc.* **1957**, 1958. (b) Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136. (c) Mihelich, E. D.; Daniels, K.; Eickhoff, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 7690. (d) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765. Cyclopropanation: (e) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256. (f) Mohamadi, F.; Still, W. C. *Tetrahedron Lett.* **1986**, *27*, 893. (g) Molander, G. A.; Etter, J. B. *J. Org. Chem.* **1987**, *52*, 3942. (h) Molander, G. A.; Harring, L. S. *J. Org. Chem.* **1989**, *54*, 3525.

(3) For attempted hydrogenation of vinylstannanes, see: (a) Mitchell, T. N. *J. Organomet. Chem.*, **1986**, *304*, 1. and (b) Jousseaume, B. *J. Chem. Soc. Chem. Commun.* **1984**, 1452. For the reaction with diimide, see: (c) Rahm, A.; Grimeau, J.; Petraud, M.; Barbe, B. *J. Organomet. Chem.* **1985**, *286*, 297. For a hydrogenation of an arylsilane using Rh/C, see: (d) Kitching, W.; Olszowy, H. A.; Drew, G. M.; Adcock, W. *J. Org. Chem.* **1982**, *47*, 5153. (e) Takeuchi, R.; Sugiura, M. *J. Chem. Soc. Perkin Trans. 1* **1993**, 1031.

(4) Dimetalated compounds have found increasing utility in organic synthesis, see: (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Tanaka, K.; Uneme, H.; Matsui, K. S.; Tanikaga, R.; Kaji, A. *Chem. Lett.* **1980**, 287. (c) Halazy, S.; Dumont, W.; Krief, A. *Tetrahedron Lett.* **1981**, *22*, 4737. (d) Eisch, J. J.; Piotrowski, A. *Tetrahedron Lett.* **1983**, *24*, 2043. (e) Mitchell, T. N.; Reimann, W. *J. Organomet. Chem.* **1985**, *281*, 163. (f) Knochel, P.; Normant, J. F. *Tetrahedron Lett.* **1986**, *27*, 1039, 1043, 4427, 4431, 5727. (g) Mitchell, T. N.; Reimann, W. *J. Organomet. Chem.* **1987**, *322*, 141. (h) Krief, A.; Evrard, G.; Badaoui, E.; De Beys, V.; Dieden, R. *Tetrahedron Lett.* **1989**, *30*, 5635. (i) Magriotis, P. A.; Doyle T. J.; Kim, K.D. *Tetrahedron Lett.* **1990**, *31*, 2541. (j) Lautens, M.; Huboux, A. H.; Chin, B.; Downer, J. *Tetrahedron Lett.* **1991**, *31*, 5829. (k) Barrett, A. G. M.; Hill, J. M. *Tetrahedron Lett.* **1991**, *32*, 3285. (l) Magriotis, P. A.; Brown, J. T.; Scott, M. E. *Tetrahedron Lett.* **1991**, *32*, 5047. (m) Barrett, A. G. M.; Hill, J. M.; Wallace, E. M.; Flygare, J. A. *Synlett* **1991**, 764. (n) Pine, S. H.; Shen, G. S.; Hoang, H. *Synthesis* **1991**, 165. (o) Marek, I.; Lefrançois J.-M.; Normant, J. F. *Tetrahedron Lett.* **1991**, *32*, 5969. (p) Marek, I.; Normant, J. F. *Tetrahedron Lett.* **1991**, *32*, 5973. (p) Tucker, C. E.; Knochel P. *J. Am. Chem. Soc.* **1991**, *113*, 9888. For a recent review, see: Normant, J. F.; Marek, I.; Lefrançois, J.-M. *Pure and Appl. Chem.* **1992**, *64*, 1857.

(5) For a preliminary account of this work, see: Lautens, M.; Zhang, C. M.; Crudden, C. M. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 232. *Angew. Chem.* **1992**, *104*, 237.

(6) Thompson, H. W. *J. Org. Chem.* **1971**, *36*, 2577. For a review of the directed hydrogenation, see: Brown, J. M. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 190.

(7) (a) Brown, J. M.; Naik, R. G. *J. Chem. Soc. Chem. Commun.* **1982**, 348. (b) Brown, J. M.; Hall, S. A.; *J. Organomet. Chem.* **1985**, *285*, 333. (c) Crabtree, R.H.; Davis, M. W. *Organometallics* **1983**, *2*, 681. (d) Crabtree, R. H.; Davis, M.W. *J. Org. Chem.* **1986**, *51*, 2655. (e) Stork, G.; Kahne, D. E. *J. Am. Chem. Soc.* **1983**, *105*, 1072. (f) Evans, D. A.; Morrissey, M. M. *J. Am. Chem. Soc.* **1984**, *106*, 3866. (g) Evans, D. A.; Morrissey, M. M. *Tetrahedron Lett.* **1984**, *25*, 4637. (h) Evans, D. A.; Morrissey, M. M.; Dow, R. L. Tetrahedron *Lett.* **1985**, *26*, 6005. (i) Evans, D. A.; DiMare, M. *J. Am. Chem. Soc.* **1986**, *108*, 2476.

0022-3263/94/1959-6208$04.50/0

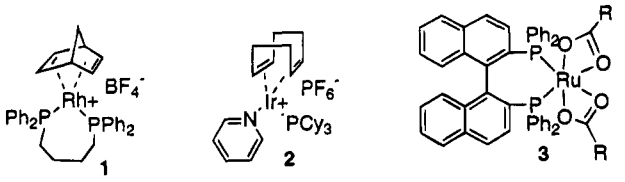


Figure 1.

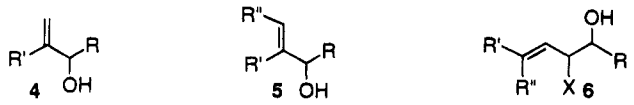


Figure 2.

tion metal catalysts based on rhodium (e.g. (dppb)-$Rh^+(NBD)BF_4^-$, **1**) and Crabtree's iridium complex ($(1,5\text{-}COD)(Cy_3P)Ir^+(pyr)PF_6^-$, **2**) were found to be most effective for achieving high diastereoselectivity. Noyori and Takaya have shown that chiral BINAP-Ru dicarboxylate complexes **3** are highly reactive catalysts for the directed hydrogenation of *achiral* acyclic allylic and homoallylic alcohols.[8]

The majority of substrates which had been examined when we initiated our studies fell into three categories; 1,1-disubstituted olefins **4**, 1,1,2-trisubstituted olefins **5**, and homoallylic alcohols of general structure **6**.[7f] The substituents R, R′, and R″ included alkyl, oxygen, and nitrogen moieties.[9] The feasibility and diastereoselectivity of hydrogenating olefins bearing other substituents had not been explored despite the synthetic potential of the products.[9]

Contemporary with our work were studies by Brown and co-workers on the reduction of alkenes bearing sulfur derivatives where similar questions of reactivity were examined. They found that reduction of vinyl sulfoxides or sulfones was efficient but gave different stereochemical results. The allylic hydroxyl group directs the reduction in a vinyl sulfone, but the S—O bond of the sulfoxide is dominant in the sulfoxide series.[10]

Preparation of Starting Materials

The starting vinylmetallic species **A**–**D** used in this study were prepared by literature routes and modifications developed by us. Compounds of general structures **A** (**7**, **8**, **11**, **14**, **16**, and **18**, Table 1) were generated using our recently reported hydrometalation–stannation sequence.[11] Thus, a propargyl alcohol bearing an alkyl substituent (R′ = alkyl) was added to a premixed suspension of "Cp_2TiH" (prepared by adding 2 equiv of *i*-BuMgCl

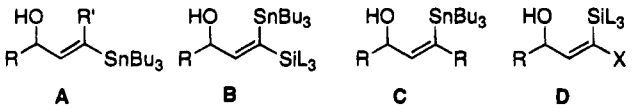
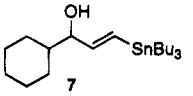
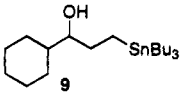
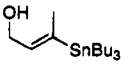
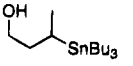
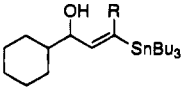
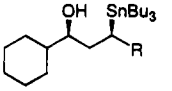
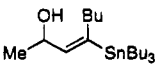
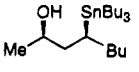
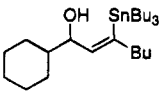
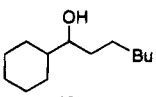
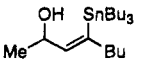
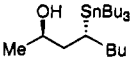


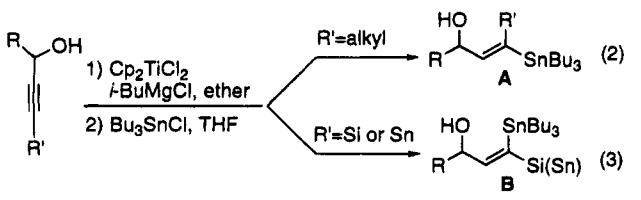
Figure 3.

Table 1. Directed Hydrogenation of γ-Hydroxy Vinylstannanes

Entry	Substrate	Product[a]	Yield[b] (*syn:anti ratio*)
1	 **7**	 **9**	67%[c]
2	 **8**	 **10**	59[d]
3			
	a) **11** R=*n*-Bu	**12** R=*n*-Bu	70%[e] (>100:1)
			85%[f] (>100:1)
	b) **14** R=*i*-Pr	**15** R=*i*-Pr	83% (300:1)
	c) **16** R=*t*-Bu	**17** R=*t*-Bu	70%[d, g]
4	 **18**	 **19**	95% (>100:1)
5	 **20**	 **13**	see text
6	 **21**	 **22**	50% (>100:1)

a. Typical reaction conditions involve treatment of the substrate with **1** (5 mol%) at 1400-1500 psi in CH_2Cl_2 for 24-36h. b. Isolated yield of pure product following flash chromatography. c. Plus 17% recovered starting material. c. Unoptimized yield. e. Approximately 13% of **13** was isolated using 17 mol% of **1**. f. Approximately 3% of **13** was isolated using 5 mol% of **1**. g. The minor isomer could not be detected.

to titanocene dichloride). Hydrotitanation of the alkyne and subsequent titanium–magnesium exchange gives a vinylmagnesium intermediate which is trapped with tributyltin chloride, eq 2.[12,13] This hydrometalation is catalytic in titanium and is stereoselective, furnishing exclusively the (*E*)-isomer, **A**. It is essential to change the solvent from ether to THF following the hydromagnesiation reaction in order to obtain high yields of the stannylated product.



For those alkynes bearing a silicon or tin substituent (R′ = Si or Sn), trapping with tributyltin chloride under

(8) (a) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (b) Takaya, H.; Ohta, T.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Inoue, S.; Kasahara, I.; Noyori, R. *J. Am. Chem. Soc.* **1987**, *109*, 1596, 4129. (c) Kitamura, M.; Nagai, K.; Hsiao, Y; Noyori, R. *Tetrahedron Lett.* **1990**, *31*, 549. For a recent review of this field, see: Noyori, R. *Asymmetric Catalysis in Organic Synthesis* Wiley Interscience: Toronto, 1994. Takaya, H.; Ohta, T.; Noyori, R. *Catalytic Asymmetric Synthesis*. Ojima, I., Ed.; VCH, New York, 1993; p 1–39.

(9) Hydrogenation of olefins bearing heteroatoms are known. One of the most useful examples is the asymmetric hydrogenation of α-(acylamido)cinnamic acid derivatives. However, the hydroxyl group does not control the facial selectivity of the process and, most relevant to our work, the olefin does not bear a heteroatom which is a metaloid such as tin or silicon. For a discussion of the hydrogenation and further references, see: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(10) Ando, D.; Bevan, C.; Brown, J. M.; Price, D. W. *J. Chem. Soc. Chem. Commun.* **1992**, 592.

(11) Lautens, M.; Huboux, A. H. *Tetrahedron Lett.* **1990**, *31*, 3105.

Table 2. Directed Hydrogenation of γ-Hydroxy Vinylsilanes

Entry	Substrate	Product[a]	Yield[b] (*syn:anti ratio*)
1	**24a** R H, R'=$PhMe_2Si$	**25**	99%
2	**24b** R=$PhMe_2Si$, R'=H		90%
3	**26** R=Me, R'=$PhMe_2Si$	**28** R=Me, R'=$PhMe_2Si$	99% (>500:1)
4	**27** R=$PhMe_2Si$, R'=Me	**29** R=$PhMe_2Si$, R'=Me	95% (1:>500)
5	**30**	**31**	93%[c]
6	**32**	**33**	95%[c,d]

a. Typical reaction conditions involve treatment of the substrate with 5 mol% **1** in CH_2Cl_2 for 24-48h at 1500 psi. b. Isolated yield of pure product following flash chromatography. c. Only one isomer observed. d. Both **32** and **33** (Me) were contaminated with some **32** and **33** (H) which could not be separated by flash chromatography.

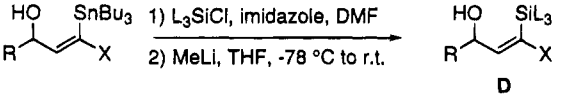
identical conditions gives the stereoisomeric compounds corresponding to **B** (i.e. **35**–**41**, and **44**, Table 3) since the initially formed vinylmagnesium intermediate isomerizes to the more stable (*Z*)-isomer, eq 3.[13a-c] Trapping with a proton or an alkyl halide gives (*E*)-vinylsilanes **24a** and **26** as previously described by Sato.[13a-c]

Compounds **20** and **21** (i.e. class **C**) are prepared in two steps via a conjugate addition of a tributyl tin moiety (Bu_6Sn_2, $(Ph_3P)_4Pd$) to an ynone as described by Piers[14] followed by reduction of the β-stannyl enone ($NaBH_4$, $CeCl_3$) to yield the (*Z*)-allylic alcohol. A hydroboration–alkylation sequence on an acetylenic silane was used to prepare **27**.[21] Compounds **D** where X = alkyl, Si, Sn (i.e. **42**, **43**, and **45**) are prepared by the use of a 1,4-silyl migration reaction.[15] Thus, conversion of **B** or **C** to a silyl ether (L_3SiCl, imidazole, DMF) and treatment with MeLi leads to a tin–lithium exchange and stereospecific 1,4-migration of the silicon group.[15,16] Compound **30** was prepared by hydroalumination of the propargyl alcohol, iodination, and silyl migration as reported by Magriotis.[16a]

Table 3. Directed Hydrogenation of Dimetalated Olefins

Entry	Substrate	Product[a]	Yield[b]
1	**35** R=H, Si=TMS	**46** R H, Si=TMS	99%
2	**36** R=Me, Si=DMPS	**47** R=Me, Si=DMPS	99%
3	**37** R=Me, Si=TMS	**48** R=Me, Si=TMS	96%
4	**38** R=$MeOCH_2$, Si=TMS	**49** R=$MeOCH_2$, Si=TMS	94%
5	**39** R=*n*-Pr, Si=TMS	**50** R=*n*-Pr, Si=TMS	91%
6	**40** R=*i*-Pr, Si=TMS	**51**	0%[c]
7	**41** R=C_6H_{11}, Si=TMS	**52**	0%[c]
8	**42** R=TMS	**53** R=TMS	quant.
9	**43** R=$SnBu_3$	**54** R=$SnBu_3$	98%
10	**44**	**55**	55%[d]
11	**45**	**56**	87%

a. Typical reaction conditions involve treatment of the substrate with 5 mol% **1** in CH_2Cl_2 for 16-48h at 1500 psi. b. Isolated yield of pure product. c. A 40% yield of the destannated product shown was isolated. d. A 12% yield of the monodestannated product was also isolated.



D

Figure 4.

Hydrogenation Results

Stannanes **7** and **8**, Table 1, entries 1, 2, were chosen for preliminary experiments to establish the optimum conditions for hydrogenation of di- or trisubstituted olefins without the additional complications of determining the diastereoselectivity. Initially, hydrogenation was attempted under previously described conditions (1–3 mol % catalyst, 600 psi), but we observed virtually no reaction. This confirmed that vinylstannanes react more slowly than their carbon analogues. However, treatment of **7** or **8** with 5–17 mol % of **1** in dichloromethane under ca. 1400–1500 psi of hydrogen for 24–48 h resulted in complete consumption of the starting material. Removal of the catalyst by filtration through a plug of silica followed by flash chromatography provided the hydrogenated products **9** and **10** in good yield.

Having established the viability of the overall reaction, the facial selectivity of the directed hydrogenation to the diastereotopic faces of vinylstannane **11** was examined. Using 17 mol % of catalyst **1** at 1400 psi for 36 h, alkylstannane **12** was isolated in 70% yield along with an additional product **13** in which hydrogenolysis of the

(12) For studies on the hydrometalation of simple silylacetylenes catalyzed by titanium without isomerization, see: Rossi, R.; Carpita, A.; Bellina, F.; De Santis, M.; Veracini, C. A. *Gazz. Chim. Ital.* **1990**, *120*, 457.

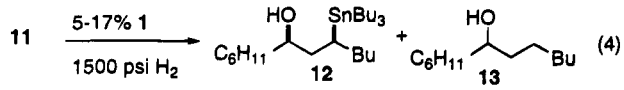
(13) The hydromagnesiation of a propargyl alcohol catalyzed by titanium was first reported by Sato, see: (a) Sato, F. *J. Organomet. Chem.* **1985**, *285*, 53. (b) Sato, F.; Watanabe, H.; Tanaka, Y.; Sato, M. *J. Chem. Soc. Chem. Commun.* **1982**, 1126. (c) Sato, F.; Kobayashi, Y. *Org. Synth.* **1990**, *69*, 106. For information on the mechanism of the hydrotitanation reaction, see: Martin, H. A.; Jellinek, F. *J. Organomet. Chem.* **1967**, *8*, 115. *Ibid.* **1966**, *6*, 293.

(14) (a) Piers, E.; Tillyer, R. D. *J. Chem. Soc. Perkin Trans. 1* **1989**, 2124. (b) Gemal, A. L.; Luche, J.-L. *J. Am. Chem. Soc.* **1981**, *103*, 5454.

(15) (a) Speier, J. L. *J. Am. Chem. Soc.* **1952**, *74*, 1003. (b) Brook, A. G.; Pascoe, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 6224. (c) Evans, D. A.; Takacs, J. M.; Hurst, K. M. *J. Am. Chem. Soc.* **1979**, *101*, 371. (d) Mora, J.; Costa, A. *Tetrahedron Lett.* **1984**, *25*, 3493. (e) Rucker, C. *Tetrahedron Lett.* **1984**, *25*, 4349. (f) Bures, E. J.; Keay, B. A. *Tetrahedron Lett.* **1987**, *28*, 5965. (g) Linderman, R. J.; Ghannam, A. *J. Am. Chem. Soc.* **1990**, *112*, 2392 and references therein.

(16) (a) Kim, K. D.; Magriotis, P. A. *Tetrahedron Lett.* **1990**, *43*, 6137. (b) Lautens, M.; Delanghe, P. H. M.; Goh, J. B.; Zhang, C. H. *J. Org. Chem.* **1992**, *57*, 3270 and references therein. See also, Hoffmann, R.; Bruckner, R. *Chem. Ber.* **1992**, *125*, 2731 for further discussion of the stereochemistry of silyl migrations in acyclic systems.

vinylstannane and hydrogenation of the olefin had occurred (ca. 13%), eq 4. By reducing the amount of catalyst to 5 mol % and increasing the pressure to 1500 psi, the yield of **12** improved to 85% with only 3% of **13**. The crude reaction mixture was examined by ^{1}H, ^{13}C, and

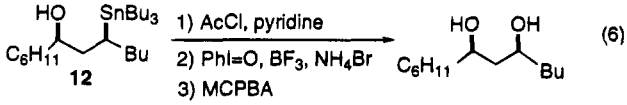


(4)

^{119}Sn NMR to evaluate the diastereoselectivity. Each of the spectra showed only one set of resonances. In light of the possibility of coincidental overlap of the signals, we prepared an authentic mixture of the diastereomers by oxidation of the hydroxystannane to the corresponding ketone with PDC (82%) followed by nonselective reduction with $NaBH_4$ (97%), eq 5. The ^{119}Sn NMR of the mixture showed two resonances at −10.6 ppm and −13.5 ppm in a 5:1 ratio. The major signal was identical to that of the starting hydroxystannane **12**, and the minor signal was assigned to its diastereomer **23**. Conditions were established for separation of the diastereomers by HPLC to facilitate determination of the diastereoselectivity of the crude hydrogenation mixture. For the conversion of **11** to **12**, the diastereoselectivity was determined to be >100:1.

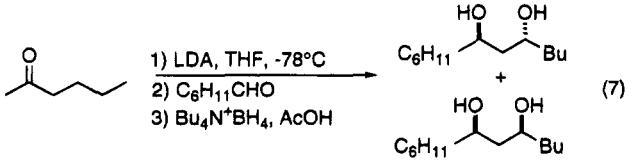
(5)

Despite obtaining excellent selectivity, we were unable to directly determine the sense of the diastereoselectivity (i.e. *syn* or *anti*) since this compound had not previously been reported. In order to correlate the stereochemistry of the hydroxystannane to a known compound, the carbon−tin bond was oxidized to a carbon−oxygen bond with retention of stereochemistry via the two-step procedure reported by Ochiai, eq 6.[17] An authentic sample of the diol was prepared by aldol condensation of the



(6)

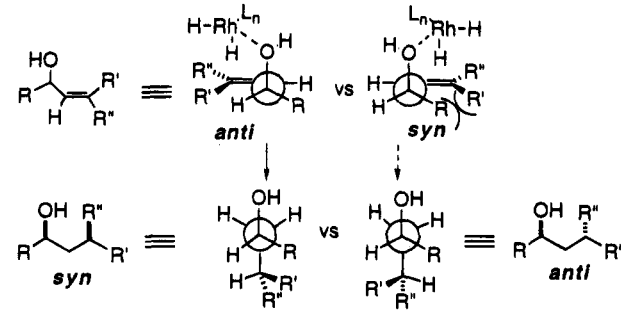
kinetic enolate of 2-hexanone with cyclohexane carboxaldehyde followed by a hydroxyl-directed reduction[18] which gave a 4:1 mixture of the *anti*:*syn* 1,3-diol, eq 7. The ^{13}C NMR spectra of the diol prepared from the



(7)

oxidation of the C−Sn bond showed chemical shifts at 77.6 and 73.4 ppm for the two carbinol carbons. The major diol (i.e. *anti*) prepared from the directed reduction (eq 7) showed signals at 73.1 and 69.3 ppm while the minor isomer's resonances were observed at 77.6 and 73.3 ppm. Thus we can conclusively establish that the *syn* hydroxystannane is produced in the hydrogenation. These diols follow the usual trend in ^{13}C NMR spectra, namely that the carbinol carbons appear upfield in the *anti* isomer compared to the *syn* isomer.[19,20]

Scheme 1



The selective formation of this product can be understood by analysis of the Newman projections designated *syn* and *anti* representing the reactive conformations, Scheme 1. Nonbonded steric interactions between the R and R′ group favor the *anti* conformer which leads to the observed syn product. Additional substrates **18**, **14**, and **16**, bearing increasingly bulky substituents R, were prepared and subjected to the hydrogenation conditions with catalyst **1**. Only one isomer was detected in each case.

Hydrogenation of (*Z*)-vinylstannanes **20** and **21** was also examined with surprising results. The size of the substituent attached to the carbinol carbon clearly plays an important role in determining the course of the reaction. Firstly, reaction of **20** with 5 mol % of **1** was much slower compared to stannane **11**, returning primarily starting material (80%) along with 20% of the reductively destannated product **13**. If the amount of catalyst was increased to 20 mol % the major product was **13** (45%) plus unreacted starting material (20%) (Table 1, entry 5).[10] However, if the cyclohexyl group was replaced by a methyl group, then hydrogenation occurred to provide **22** in 51% yield accompanied by some destannated product (~10%), entry 6. This change from hydrogenation to destannation as a function of substituent at the carbinol carbon in the (*Z*)-isomer is quite general. A similar effect was also noted upon changing the steric size of the R″ group for the 1,1-dimetalated compounds shown in Table 3, *vide infra*.

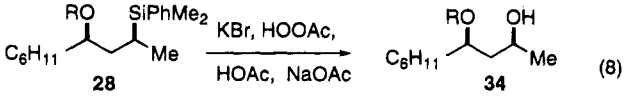
The reactivity and selectivity of (*E*) and (*Z*)-vinylsilanes toward hydrogenation was also studied. We anticipated that reductive desilylation was less likely and therefore the hydrogenation should be less sensitive to the stereochemistry of the substituent and the steric bulk at the carbinol carbon. Our results support this idea since hydrogenation of both isomers of the γ-hydroxy vinylsilanes was extremely clean and high yielding. Upon

(17) The oxidation of C−Sn to C−O has been shown to occur with retention of configuration, see: (a) Ochiai, M.; Iwaki, S.; Ukita, T.; Matsuura, Y.; Shiro, M.; Nagao, Y. *J. Am. Chem. Soc.*, **1988**, *110*, 4606. (b) Herndon, J. W.; Wu, C. *Tetrahedron Lett.* **1989**, *30*, 6461. While the yield of the oxidation in our hands was only 15%, the high selectivity of the hydrogenation process insured that we were examining the diol from the major diastereomer.

(18) Evans, D. A.; Chapman, K. T.; Carreira, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 3560. Much higher selectivities are possible using this methodology than those reported here but our intention was to generate *both* isomers in sufficient amounts that they could be observed by ^{13}C NMR and CGC (trimethylsilyl ethers) while remaining certain of which isomer would predominate. For other methods of carrying out directed reductions of β-hydroxy ketones, see: (a) Narasaka, K.; Pai, F.-C. *Tetrahedron* **1984**, *40*, 2233. (b) Chen, K.-M.; Hardtmann, G. E.; Prasad, K.; Repic, O.; Shapiro, M. J. *Tetrahedron Lett.* **1987**, *28*, 155.

treatment of **24a,b**, **26**, and **27**[21] with catalyst **1** for 48 h, the saturated silanes **25**, **28**, and **29** were isolated in >90% yields, Table 2. Exceptionally high diastereoselectivities (>500:1) were obtained for **28** and **29**.

Conversion of the sp^3 C—Si bond to a carbon—oxygen bond with retention of stereochemistry under very mild conditions illustrates how the alkylsilane produced in the hydrogenation can be utilized in synthesis. For example, oxidation of **28** using the Fleming procedure gave a *syn* 1,3-diol **34** (R = H) in 68% yield, eq 8.[22] The relative stereochemistry of the hydroxyl groups was proven by independent synthesis of both the *syn* and *anti* isomers and comparison of their ^{13}C NMR spectra.[19,20] One feature of this strategy is the facile preparation of differentially protected diols.[23] For example, protection of the hydroxyl group of **28** as the methyl ether prior to oxidation gave the differentially protected 1,3-diol **34** (R = Me) in 71% yield.



(8)

Hydrogenation of Heterobimetallic Compounds

The hydrogenation of heterobimetallic compounds bearing tin and silicon, two silicons, or two tins was also studied, Table 3, entries 1—11. Hydrogenation is facile for these compounds, but as we observed with **18**, **20**, and **21**, the course of the reaction depends on the size of the substituent R. When R is a hydrogen or straight chain alkyl group, i.e. **35—39**, the diastereomerically pure hydrogenation products **46—50** were isolated in very high yields. However, branched chain substituents, i.e. **40** and **41**, undergo destannation and hydrogenation giving **51** and **52** in 40% yield with the balance being recovered starting stannyl alkene. The diastereoselectivity in the formation of **47** was determined to be ca. 60:1 by HPLC while the minor diastereomer could not be detected in the other substrates. The sense of diastereoselection was assumed to be identical to that previously observed for the silanes and stannanes.

Homobimetallic compounds also undergo hydrogenation of the alkene. Disilyl alkene **42** gave **53** in quantitative yield and the distannyl alkene **44** gave **55** in 55% yield. In the former example, a new stereocenter bearing two different silicon groups was created. This methodology provides efficient access to diastereomerically pure, 1,1-dimetalated compounds in only two or three steps from a propargyl alcohol.[10] Since propargyl alcohols are readily prepared in enantiomerically pure form, the directed reduction reactions described here should make homochiral 1,1-heterobimetallic compounds available for further study as reagents in synthesis.[24]

Table 4 lists representative ^{119}Sn NMR chemical shifts for the vinylstannanes and for the diastereomerically pure hydroxy stannanes.

Table 4. ^{119}Sn NMR Chemical Shifts of Vinylstannanes and (Hydroxyalkyl)stannanes

compound	type	major	minor	ratio[a]
7	alkene	−46.0	na	na
9	alkane	−7.3	na	na
11	alkene	−38.1	na	na
12	alkane	−10.6	−13.5	5.0:1
14	alkene	−38.8	na	na
15	alkane	−14.6	−15.3	5.3:1
16	alkene	−25.5	na	na
17	alkane	−12.7	−16.2	5.5:1
18	alkene	−39.2	na	na
19	alkane	−10.6	−12.2	2.7:1
21	alkene	−51.6	na	na
22	alkane	−12.2	−10.6	na
35	alkene	−52.6	na	na
46	alkane	−0.13	–	–
47	alkane	−0.01	–	–
37	alkene	−53.0	na	na
48	alkane	−2.6	–	–
38	alkene	−52.0	na	na
49	alkane	−0.56	–	–
39	alkene	−54.0	na	na
50	alkane	−3.7	–	–
43	alkene	−20.1	na	na
54	alkane	−2.2	–	–
44	alkene	−22.6, −48.4	na	na
55	alkane	−8.9, −7.4	na	na

[a] The ratio of ^{119}Sn signals following oxidation of the hydroxystannane with PDC followed by reduction with $NaBH_4$.

Competition Studies

Substitution of a vinylic hydrogen or carbon by silicon and/or tin clearly inhibits the rate of hydrogenation. Significantly higher pressures are required to achieve the reduction compared to previously examined substrates. A direct comparison between silicon, tin, and carbon was therefore of interest to determine the effect of each substituent on the rate of reduction. A series of competition experiments was carried out in order to evaluate the effect of a substituent and its stereochemistry on the rate of the hydrogenation reaction.

The reactions were carried out by treating an approximately 1:1 mixture of the two substrates with 2.5—5 mol % of the cationic rhodium catalyst **1** for 15 min—1 h at 1400—1500 psi. If one substrate was found to be much more reactive than the other, then a 1.5—2:1 ratio of the less reactive:more reactive substrate was used. ^1H NMR (400 MHz) was used to determine the precise ratio of the

(19) For an analysis of ^{13}C shifts in the acetonides of 1,3-diols, see: (a) Rychnovsky, S. D.; Skalitzky, D. J. *Tetrahedron Lett.* **1990**, *31*, 945. (b) Evans, D.A.; Rieger, D. L.; Gage, J. R. *Ibid.* **1990**, *31*, 7099. (c) Rychnovsky, S. D.; Rogers, B.; Yang, G. *J. Org. Chem.* **1993**, *58*, 3511.

(20) A similar analyses has been carried out to explain the selectivity of 1,1-disubstituted olefins; however, in this case the substituent R interacts with R' making the other conformer the preferred and reactive one, see ref 7f—h.

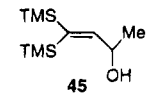
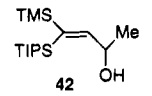
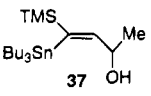
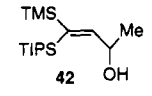
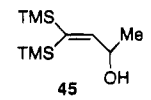
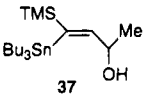
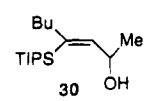
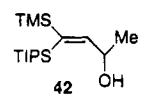
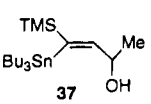
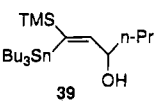
(21) Ziegler, F. E.; Mikami, K. *Tetrahedron Lett.* **1984**, *25*, 131. The principal difficulty with this procedure is separation of the protonated material from the alkylated product, see Experimental Section.

(22) Fleming, I., Sanderson, P. E. J. *Tetrahedron Lett.* **1987**, *28*, 4229. For some recent studies, see: Crump, R. A. N.; Fleming, I.; Urch, C. J. *J. Chem. Soc., Perkin Trans. 1* **1994**, 701 and references therein. For reviews on the chemistry of silicon and tin compounds in organic synthesis, see: (a) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987 and references therein. (b) Yamamoto, Y., Ed. *Organotin Compounds in Organic Synthesis.* Tetrahedron Symposia in Print No. 36. *Tetrahedron* **1989**, *45*, 909. (c) Fleming, I. *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: New York; 1991; p 1079. (d) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (e) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983. (f) Larson, G. L. *The Chemistry of Organic Silicon Compounds*, Patai, S., Ed.; Wiley Interscience: Toronto, 1989; Part 1, Chapter 11. (g) Fleming, I.; Dunogues, J.; Smithers, R. *Org. React.* **1989**, *37*, 57.

(23) For a novel route to differentially protected 1,3-diols, see: Evans, D. A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1990**, *112*, 6447 and references therein.

(24) (a) Midland, M. M.; Tramontano, A. *Tetrahedron Lett.* **1980**, *21*, 3549. (b) Noyori, R.; Tomino, I.; Yamada, M.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6717. (c) Yamaguchi, S.; Mosher, H. S.; Pohland, A. *J. Am. Chem. Soc.* **1972**, *94*, 9254. (d) Ramachandran, P. V.; Teodorovic, A. V.; Rangaishenvi, M. V.; Brown, H. C. *J. Org. Chem.* **1992**, *57*, 2379 and references therein. (d) For a recent approach, see: Corey, E. J.; Cimprich, K. A. *J. Am. Chem. Soc.* **1994**, *116*, 3151 and references therein.

Table 5. Relative Rates of Hydrogenation of Vinylmetallic Compounds

Entry	Substrate A	Substrate B	% conversion (A,B)	Relative Rate[a]
1	 **45**	 **42**	47, 2	>30
2	 **37**	 **42**	41, 2	25
3	 **45**	 **37**	33,17	2
4	 **30**	 **42**	94, 20	9
5	 **37**	 **39**	21, 11	2

a. The expression: $k_A/k_B = \ln\{[A]/[A_o]\}/\ln\{[B]/[B_o]\}$ to determine the relative rates for each pair of substrates. We thank Professor R.A. McClelland for assistance in these studies.

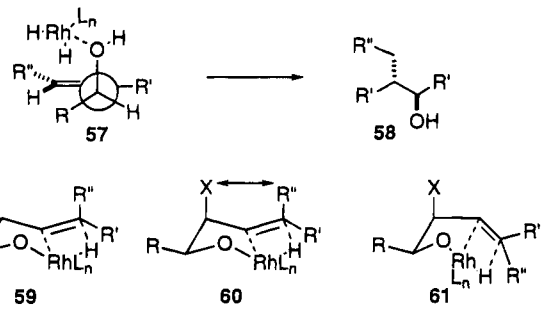
starting materials and to measure the percent conversion of each of the starting materials and the relative amounts of each hydrogenation product. One assumption is that all the starting material consumed gives exclusively the hydrogenated product. For TMS containing compounds, integration of the singlets corresponding to the CH_3Si resonances was used. For those substrates lacking a silicon (and therefore a high field signal), integration of the vinylic proton in the starting material and comparison with the carbinol proton for the starting material and product (which typically resonated at different chemical shifts) were used.

These studies reveal several trends, Table 5. In general the hydrogenation reaction is quite fast for many of the substrates at 1500 psi requiring <5% of the catalyst. As expected, steric bulk at the vinylic position clearly has a significant effect on the rate of the reaction. For example, replacement of a (*Z*)-TIPS by a TMS causes a significant increase in the rate of reaction, entry 1. Similarly, a (*Z*)-tributyltin group reacts much faster than a (*Z*)-triisopropylsilyl group but at approximately half the rate of a substrate bearing a trimethylsilyl group, entries 2 and 3. Substitution of an (*E*)-*n*-butyl group by a TMS group causes a nearly 10-fold decrease in rate, and changing the substituent attached to the carbinol carbon from methyl to *n*-propyl causes the rate to decrease by a factor of two. The aforementioned destannation process precluded continuing the study with R = *i*-Pr or *t*-Bu.[25]

Source of the Diastereoselectivity

We have shown that vinylsilanes, vinylstannanes, and olefins bearing silicon and tin undergo a highly diastereoselective hydrogenation reaction. The starting materials for the hydrogenation are readily prepared in one or two steps from simple precursors. High diastereoselectivity has been achieved leading to *syn* or *anti* hydroxy silanes and stannanes. Our studies support the importance of $A^{1,3}$-strain in controlling the facial selectivity of the hydrogenation of suitably substituted allylic alcohols and the effect of increased crowding on the rate of the reduction.

Scheme 2



The significant interaction responsible for the high diastereoselectivity in the previously studied hydrogenation reactions (i.e. **4** and **5**) occurs between the R and R′ groups ($A^{1,2}$-strain) which is minimized in rotamer **57**, Scheme 2. The product **58** contains a 1,2-*anti* stereochemical relationship. In homoallylic alcohol **6**, the hydroxyl directs the hydrogenation but the X group controls the facial selectivity of the reaction. Chair-like transition state **59** is preferred for the *anti* diastereomer but the *syn* diastereomer prefers to react via the boat form **61** rather than the chair illustrated by **60** in order to minimize $A^{1,3}$-strain.

Destannation Reactions

In several instances vinylstannanes were found to undergo a competing reaction which removes the tin moiety from the product. We have identified the structural features in the vinylstannanes which lead to this outcome. (*E*)-vinylstannanes undergo reduction as expected whereas for (*Z*)-olefins the size of the substituent R has a dramatic effect on the efficiency of hydrogenation. Large groups (i.e. R = *i*-Pr, cyclohexyl) give the destannated hydroxyalkane, whereas small R groups (R = H, Me, $MeOCH_2$, *n*-alkyl) give the desired hydroxy stannane in good to excellent yield and with good diastereoselectivity.

The decrease in selectivity and reactivity associated with increasing the size of R suggests that conformer **E** is no longer present to an appreciable level and thus the hydrogenation reaction is inhibited. The elimination of the interaction between R and the vinylic C—H bond may favor conformer **F** or **G**. In conformer **F** the alkene should be unreactive toward hydrogenation because the hydroxyl group is no longer positioned to direct the rhodium hydride species. To the extent that **G** is present, the "inside hydroxyl" may direct the rhodium to insert into the carbon–tin bond rather than reduce the alkene, *vide infra*.[26]

Several questions arise concerning the destannation reaction. (i) When does the destannation reaction occur?

(25) The electronegativity of Si and Sn are nearly identical, and each is much less than that of carbon (1.7 vs 2.5). While they have similar electronic effects, Kitching showed that Me_3Si is significantly larger than Me_3Sn (*A* value of a trimethylsilyl group is reported to be 2.5 whereas a trimethylstannyl group is only 1.06) and attributed this to longer C—Sn bonds, see: ref 3d and Kitching, W.; Doddrell, D.; Grutzner, J. B. *J. Organomet. Chem.* **1976**, *107*, C5.

(26) Discussions on reactive rotamers abound in the literature, for example see: (a) Cha, J. K.; Christ, W. J.; Kishi, Y. *Tetrahedron Lett.* **1983**, *24*, 3943, 3947. (b) Stork, G.; Kahn, M. *Tetrahedron Lett.* **1983**, *24*, 3951. (c) Houk, K. N.; Paddon-Row, M. N.; Rondan, N. G.; Wu,

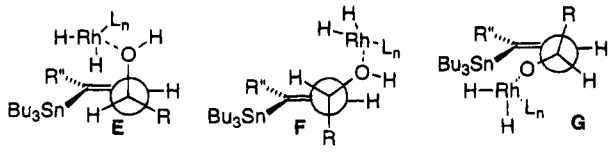


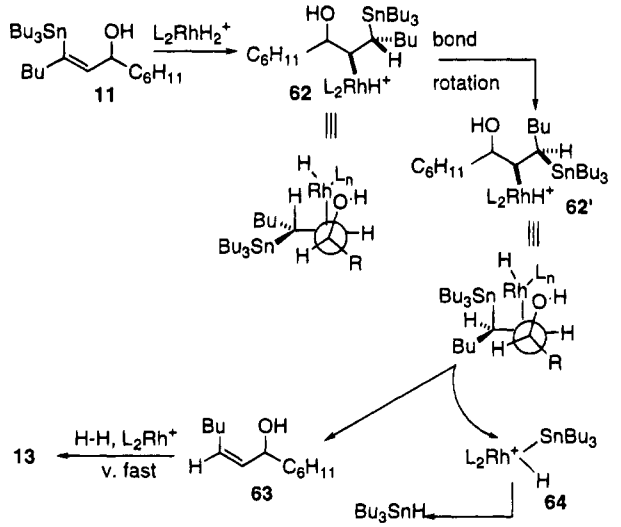
Figure 5.

(ii) Does it precede hydrogenation of the olefin? (iii) Why does the (*Z*)-stannyl olefin undergo reductive destannation more readily than the (*E*)-olefin? To probe these points the *syn* hydroxy stannane **12** was resubjected to 9 mol % of **1** under 1500 psi of hydrogen pressure. After 24 h, only 6% of **13** was isolated along with 90% recovered starting material **12**. The stability of the diastereomeric product was established when we found that alkylstannanes **19** and **22** are equally resistant to reduction of the tin moiety. These results rule out a hydroxyl-directed destannation of an *alkyl*stannane as the major destannation pathway. Thus loss of the tin must occur prior to reduction of the olefin which suggests that a destannated alkene or alkyne must be formed.

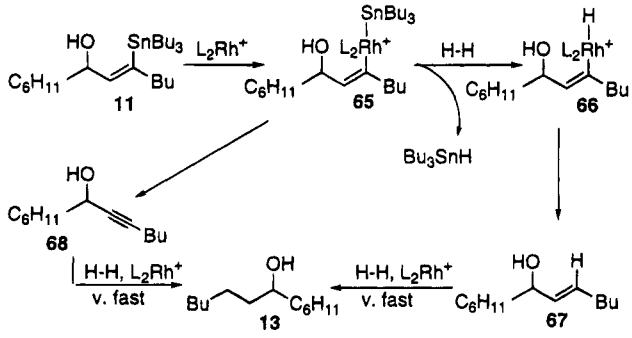
More specific information on the mechanism would be available if isolation of the olefin resulting from reductive hydrogenolysis of the carbon–tin bond was feasible. In the pathways discussed below (illustrated in Schemes 3 and 4) the stereochemistry of the destannated alkene changes from (*Z*) to (*E*) as a function of the mechanism. However, hydrogenation of carbon- or hydrogen-substituted alkenes is significantly more facile than hydrogenation of the starting material as we demonstrated earlier. Thus any alkene (or alkyne) produced from a destannation process would be rapidly reduced to the alkane under the reaction conditions.

A hydrometalation–dehydrostannation pathway yields a (*Z*)-alkene. Addition of a rhodium hydride complex to the vinylstannane would give **62** with the regiochemistry indicated. Subsequent bond rotation to **62′** followed by a *cis* β-elimination of the rhodium and tin would yield alkene **63** and a HRhSn compound **64** which would undergo reductive elimination giving Bu_3SnH. There is precedent for the reverse of these latter two reactions in the recent studies on transition metal-catalyzed hydrostannation of alkynes and dienes using Bu_3SnH in the presence of Pd(0), Rh(I), Co(II), Ru(II), and Ni(0).[27-29] However, under the conditions we have studied using hydrogen at high pressure, destannation occurs. This mechanism does not explain the different propensity for destannation in (*E*)- and (*Z*)-stannanes. The (*E*)-isomer might be predicted to undergo loss of the tin more readily

Scheme 3



Scheme 4



since the rotamer prior to β-elimination would not suffer from a nonbonded interaction between the carbinol hydrogen and the Bu group that occurs in **62′**. Furthermore, destannation of the (*E*)-isomer via the pathway would give the (*E*)-alkene **67**.

Another possible pathway is a hydroxyl directed insertion into the C–Sn bond of the vinylstannane by the cationic metal complex, as might arise from conformer **G** shown above. Under a hydrogen atmosphere, reduction of **65** to **66** and Bu_3SnH would occur followed by reductive elimination to **67**, Scheme 3. Subsequent hydrogenation of the olefin would give **13.** Implicating the hydroxyl group as a directing group in the insertion process would explain why the (*Z*)-stannane is much more prone to the destannation reaction.

A third pathway in which **65** would dehydrostannate to give propargyl alcohol **68** seems unlikely since the available data on the hydrostannation suggests that a *cis* addition predominates under metal-catalyzed conditions.[27-29]

In conclusion we have shown that vinylsilanes and stannanes can be readily hydrogenated by a cationic rhodium catalyst, that the hydroxyl group directs a selective addition to one face of the olefin with very high diastereoselectivities. Subsequent oxidation of the hydroxy silanes leads to 1,3-diols. Novel hetero- and homobimetallic compounds have been prepared in diastereomerically pure form. Destannation is a competitive process is some substrates and the structural parameters leading to this pathway have been identified. Experiments to examine the reactivity of diastereomerically enriched 1,1-dimetalated compounds are in progress.

Y.-D.; Brown, F. K.; Spellmeyer, D.C.; Metz, J. T.; Li, Y.; Loncharich, R. J. *Science* **1986**, *231*, 1108. (d) Vedejs, E.; McClure, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 1094. (e) Evans, D.A.; Kaldor, S. W. *J. Org. Chem.* **1990**, *55*, 1698.

(27) Several reports of transition metal-catalyzed hydrostannation have appeared, see: (a) Ichinose, Y.; Oda, H.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3468. (b) Kikukawa, K.; Umekawa, H.; Wada, F.; Matsuda, T. *Chem. Lett.* **1988**, 881. (c) Zhang, H. X.; Guibe, F.; Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1857. (d) Miyake, H.; Yamamura, K. *Chem. Lett.* **1992**, 1099. (e) Koerber, K.; Gore, J.; Vatele, J.-M. *Tetrahedron Lett.* **1991**, *32*, 1187. (f) Casson, S.; Kocienski, P. *Synthesis* **1993**, 1133. For a recent review, see: Mitchell, T. N. *Synthesis* **1992**, 803.

(28) A rhodium complex bearing an olefin, a hydride, and a tin moiety has been isolated and spectroscopically characterized, see: Ruiz, J.; Spencer, C. M.; Mann, B. E.; Taylor, B. F.; Maitlis, P. M. *J. Organomet. Chem.* **1987**, *325*, 253.

(29) In comparison with the hydrosilation process, little is known about the mechanism of the metal-catalyzed hydrostannation, see ref 27d. For a recent discussion on the hydrosilation, see: Brookhart, M.; Grant, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2151 and references therein.

Experimental Section

General Methods. ^1H, ^{13}C, and ^{119}Sn NMR data were collected on a Varian Gemini 200, Varian XL200, or XL400 spectrometer. ^{119}Sn spectra were referenced to tetramethylstannane as an external standard. Mass spectra were obtained using a VG70-250S instrument. HPLC was carried out on a Waters 600E chromatograph using a C18 Nova-pack column and a UV/VIS detector. Analytical thin layer chromatography (TLC) was carried out using EM Reagents 0.25-mm silica gel 60-F plates. Purification on a preparative scale was performed using flash chromatography on silica gel (230–400 mesh).[30] All solvents were distilled and dried prior to use. All reaction flasks were flame-dried under nitrogen. The cationic rhodium complex was prepared according to the method of Schrock.[31]

General Procedure for the Hydromagnesiation of Propargyl Alcohols. Cp_2TiCl_2 (10 mol %) was added to ^{i}BuMgCl (2.5 eq, 2.0 M in hexanes) in dry ether at 0 °C and the suspension was stirred for 10–20 min. The alkynol was then added via cannula as a solution in ether and the suspension stirred at 0 °C for 10–20 min. The reaction was then heated to reflux for the specified amount of time and the ether removed *in vacuo*. The solvent was replaced by an equal amount of THF and the electrophile was added at the specified temperature and stirred until the reaction was complete as judged by TLC. Workup was effected by partitioning between ether and H_2O. The aqueous layer was back extracted twice with ether and the combined organics washed once with distilled H_2O and brine. After drying over anhydrous Na_2SO_4 and removal of the volatiles *in vacuo*, the oil obtained was purified by flash chromatography on silica gel. The vinylstannanes were prepared from the propargyl alcohols using previously reported methodology.[11] Additional substrates prepared are reported below.

(*E*)-1-Cyclohexyl-3-(tributylstannyl)prop-2-enol (7). Following the general procedure, ^{i}BuMgCl (1.3 mL, 2.6 mmol) and Cp_2TiCl_2 (26 mg, 0.103 mmol) in 10 mL of ether were stirred for 15 min at 0 °C. A solution of 1-cyclohexyl-3-(tributylstannyl)prop-2-ynol (0.44 g, 1.03 mmol in 4 mL of ether) was added via cannula to the Schlenk flask. After stirring at 0 °C for 15 min and warming to room temperature, the solution was heated to reflux overnight. The ether was replaced with THF (4 mL) and excess H_2O (15 mL) was added with caution. After 1 h at reflux and cooling to room temperature, the reaction mixture was extracted and purified by column chromatography. Elution with 5% ethyl acetate in hexane provided 280 mg (63%) of the title compound. This compound and the acetylenic starting material were both sensitive to acid. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.07 (1H, d, J = 19.2 Hz), 5.96 (1H, dd, J = 19.1, 5.8 Hz), 3.98 (1H, m), 1.8–1.6 (6H, m), 1.40–1.6 (10H, m), 1.29 (6H, m), 0.80–1.20 (17H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 149.7, 128.2, 79.9, 9.3. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −46.0. IR (cm^{-1}, neat) 3382, 3311, 2957, 2851, 1463, 1451, 1377, 1096. HRMS *m/e* calculated for $C_{17}H_{33}OSn$ (M − $C_4H_9^+$): 373.1553. Found: 373.1566.

(*E*)-1-Cyclohexyl-4-methyl-3-(tributylstannyl)pent-2-enol (14). Following the general procedure, ^{i}BuMgCl (1.1 mL, 2.2 mmol) and Cp_2TiCl_2 (25 mg, 0.099 mmol) in 5 mL of ether were stirred for 10 min at 0 °C. A solution of 1-cyclohexyl-4-methylpent-2-ynol (180 mg, 0.865 mmol in 2 mL of ether) was added via cannula to the Schlenk flask. After stirring at 0 °C for 10 min and warming to room temperature, the solution was heated to reflux for 3 h. The ether was replaced with THF, and $ClSnBu_3$ (0.5 mL, 1.84 mmol) was added. After 2 h at reflux and cooling to room temperature, the reaction mixture was extracted and purified by column chromatography. Elution with 5% ethyl acetate in hexanes provided 323 mg (69%) of the title compound. ^1H NMR (200 MHz, $CDCl_3$) δ: 5.35 (1H, d, J = 8.8 Hz, $^3J_{SnC=CH}$ = 71.4 Hz, *H*C=), 4.22 (1H, t, J = 7.3 Hz), 2.98 (1H, heptet, J = 6.6 Hz), 1.95 (1H, d, J = 13.2 Hz) 0.8–2.0 (45H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.1, 139.4, 71.8, 44.0, 31.8 29.2, 27.4, 28.8, 26.6, 26.2, 26.1 24.2, 23.7, 13.7, 11.0. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −38.8. IR (cm^{-1}, neat) 3398, 3367, 2967, 2950, 1452, 1376, 1359. HRMS *m/e* calculated for $C_{20}H_{39}OSn$ (M − $C_4H_9^+$): 415.2023. Found: 415.2014.

(*E*)-1-Cyclohexyl-4,4-dimethyl-3-(tributylstannyl)pent-2-enol (16). Following the general procedure, ^{i}BuMgCl (1.25 mL, 2.5 mmol) and Cp_2TiCl_2 (25 mg, 0.1 mmol) in 5 mL of ether were stirred for 10 min at 0 °C. A solution of 1-cyclohexyl-4,4-dimethylpent-2-ynol (194 mg, 1.0 mmol in 2 mL of ether) was added via cannula to the Schlenk flask. After stirring at 0 °C for 5 min and warming to room temperature, the solution was heated to reflux for 2.5 h. The ether was replaced with THF and $ClSnBu_3$ (0.34 mL, 1.2 mmol) was added. After heating to reflux overnight and cooling to room temperature, the reaction mixture was extracted and purified by column chromatography. Elution with 5% ethyl acetate in hexanes provided 195 mg (40%) of the title compound. ^1H NMR (400 MHz, $CDCl_3$) δ: 5.35 (1H, d, J = 9.7 Hz, $^3J_{SnC=CH}$ = 83.8 Hz), 4.33 (1H, m), 1.98 (1H, d, J = 13.2 Hz), 0.8–2.0 (47H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 159.0, 141.7, 72.6, 44.4, 37.6, 32.9, 29.0, 27.3, 29.2, 28.6, 26.7, 26.4, 26.2, 13.5, 11.7. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −25.5. IR (cm^{-1}, neat) 3479,2950, 2850, 1451, 1376, 1360, 1077, 607. HRMS *m/e* calculated for $C_{21}H_{41}OSn$ (M − $C_4H_9^+$): 429.2179. Found: 429.2168. Anal. Calcd for $C_{25}H_{50}OSn$: C, 61.16; H, 10.37. Found: C, 61.52; H, 10.26.

(*E*)-4-(Tributylstannyl)oct-3-en-2-ol (18). Following the general procedure, ^{i}BuMgCl (3.4 mL, 7.5 mmol) and Cp_2TiCl_2 (75 mg, 0.3 mmol) in 5 mL of ether were stirred for 15 min at 0 °C. A solution of oct-3-yn-2-ol (378 mg, 3.0 mmol in 3 mL of ether) was added via cannula to the Schlenk flask. After stirring at 0 °C for 15 min and warming to room temperature, the solution was heated to reflux overnight. The ether was replaced with THF and $ClSnBu_3$ (0.97 mL, 3.3 mmol) was added. After 1 h at reflux and cooling to room temperature, the reaction mixture was extracted and purified by column chromatography. Elution with 5% ethyl acetate in hexanes provided **18** in 31.5% unoptimized yield (394 mg, 0.94 mmol). ^1H NMR (200 MHz, $CDCl_3$) δ: 5.50 (1H, d, J = 8.14 Hz, $^3J_{SnC-CH}$ = 71.4 Hz), 4.71 (1H, m), 2.25 (2H, brs), 1.2–1.7 (m, 20H), 0.7–0.9 (18H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 146.5, 144.4, 63.5, 33.1, 32.5, 28.9, 27.2, 23.4, 13.7, 13.4, 9.4. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −39.2. IR (cm^{-1}, neat) 3334, 2958, 2907, 1373, 1118. HRMS *m/e* calculated for $C_{16}H_{33}OSn$ (M − $C_4H_9^+$): 361.1553. Found: 361.1551.

(*Z*)-1-Cyclohexyl-3-(tributylstannyl)hept-2-enol (20). A solution of 1-cyclohexylhept-2-ynone (384 mg, 2 mmol) in 5 mL of THF was added via cannula to a flask containing $Pd(PPh_3)_4$ (150 mg, 0.13 mmol),[14] followed by the addition of a solution of bis(tributyltin) (1 mL, 2 mmol) in 3 mL of THF. The yellow solution formed was heated to reflux under nitrogen for 10 h to give a brown mixture which was stirred at room temperature for 36 h. The reaction mixture was then filtered through a small amount of silica gel (2 g) and eluted with 10 mL of THF. After removal of volatiles, the 1-cyclohexyl-3-(tributylstannyl)hept-2-enone (329 mg, 34%) was isolated by column chromatography (hexane, then 2.5% ethyl acetate in hexane) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.80 (1H, s, $^3J_{Sn-H}$ = 113 Hz), 2.41–2.25 (2H, m), 1.85–0.75 (45H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 203.3, 176.6, 134.7, 50.5, 40.1, 31.4, 29.2, 28.4, 27.3, 25.8, 25.6, 22.3, 13.8, 13.5, 10.8. IR (cm^{-1}, neat) 2958, 2929, 2869, 1672, 1566,1462,1451. HRMS *m/e* calcd for $C_{21}H_{41}OSn$ (M − $C_4H_9^+$): 427.2023. Found: 427.2024.

A mixture of 1-cyclohexyl-3-(tributylstannyl)hept-2-enone (171 mg, 0.36 mmol) and $CeCl_3 \cdot H_2O$ (142 mg, 0.36 mmol) in 4 mL of methanol was cooled to 0 °C. $NaBH_4$ (250 mg, 6.57 mmol) was added in two portions and the reaction mixture was stirred for 20 min after warming to room temperature. The mixture was diluted with ether and washed with aqueous HCl, H_2O, and brine. The organic phase was dried over $MgSO_4$ and volatiles were removed under reduced pressure. The product was purified by flash chromatography. Elution with 10% ethyl acetate in hexanes provided 121 mg (70%) of the title compound. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.02 (1H, d, J = 8.8 Hz, $^3J_{Sn-H}$ = 130 Hz), 3.54–3.50 (1H, m), 2.20–2.13 (2H, m), 1.90 (1H, d, J = 12.1 Hz), 1.80–0.70 (45H, m). ^{13}C NMR

(30) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(31) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397.

(50 MHz, $CDCl_3$) δ: 149.7, 141.6, 78.9, 43.8, 40.3, 32.4, 29.2, 29.1, 28.6, 27.3, 26.4, 26.1, 25.9, 22.2, 13.7, 13.4, 10.5. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −54.15. IR (cm^{-1}, neat) 3460, 2955, 2924, 2870, 1463, 1451. HRMS *m/e* calcd for $C_{25}H_{49}OSn$ ($M - H^+$): 485.2805. Found: 485.2831.

(Z)-4-(Tributylstannyl)octan-3-en-2-ol (21). A solution of 1-cyclohexylhept-2-ynone (248 mg, 2 mmol) in 5 mL of THF was added via cannula to a flask charged with $Pd(PPh_3)_4$ (128 mg, 0.1 mmol) followed by the addition of a solution of bis-(tributyltin) (1 mL, 2 mmol) in 3 mL of THF. The resulting yellow solution was heated at reflux for 22 h to give a brown mixture. The reaction mixture was then filtered through a small amount of silica gel (2 g) and eluted with 10 mL of THF. After removal of volatiles, flash chromatography (hexane, then 2.5% ethyl acetate in hexanes) provided 683 mg (82%) of (*Z*)-4-(tributylstannyl)octan-3-en-2-one as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.78 (1H, s, $^3J_{Sn-H}$ = 110 Hz), 2.39−2.35 (2H, m), 2.19 (3H, s), 1.50−1.16, 0.95−0.80 (34H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 197.9, 177.7, 135.5, 39.9, 31.3, 29.9, 22.3, 13.7, 29.2, 27.4, 13.5, 10.9. IR (cm^{-1}, neat) 2980, 2924, 2854, 1687, 1574, 1461, 1201. HRMS *m/e* calcd for $C_{16}H_{31}OSn$ ($M - C_4H_9^+$): 359.1397. Found: 359.1390.

A mixture of (*Z*)-4-(tributylstannyl)octan-3-en-2-one (200 mg, 0.5 mmol) and $CeCl_3 \cdot H_2O$ (240 mg, 0.6 mmol) in 4 mL of methanol was cooled to 0 °C. $NaBH_4$ (250 mg, 6.6 mmol) was added and the reaction mixture was stirred for 20 min before the addition of another portion of $NaBH_4$ (120 mg, 3.2 mmol). After stirring for another 20 min, the mixture was diluted with ether and washed with aqueous HCl, H_2O, and brine. The organic phase was dried over $MgSO_4$, the volatiles were removed and the product was purified by flash chromatography. Elution with 10% ethyl acetate in hexanes provided 147 mg (73%) of **21**. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.00 (1H, d, *J* = 8.6 Hz, $^3J_{Sn-H}$ = 127 Hz), 4.09−4.01 (1H, m), 2.29−1.97 (2H, m), 1.54−1.17, 1.01−0.76 (38H, 2m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 147.3, 143.8, 70.9, 39.9, 32.3, 23.4, 22.1, 13.8, 29.1, 27.2, 13.4, 10.4. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −51.56. IR (cm^{-1}, neat) 3360, 2945, 2917, 2854, 1462, 1370,1054. HRMS *m/e* calcd for $C_{16}H_{33}OSn$ ($M - C_4H_9^+$): 361.1553. Found: 361.1540.

(E)-1-Cyclohexyl-3-(dimethylphenylsilyl)prop-2-enol (24a). Following the general procedure for hydromagnesiation, ^{i}BuMgCl (0.6 mL, 1.2 mmol) and Cp_2TiCl_2 (12 mg, 0.047 mmol) in 10 mL of ether were stirred for 15 min at 0 °C. A solution of 1-cyclohexyl-3-(dimethylphenylsilyl)prop-2-ynol (130 mg, 0.48 mmol) in 3 mL of ether was added via cannula to the Schlenk flask. After stirring at 0 °C for 15 min and warming to room temperature, the solution was heated to reflux overnight. The ether was replaced with THF and excess H_2O (15 mL) was added with caution. After 1 h at reflux and cooling to room temperature, the reaction mixture was extracted and purified by column chromatography. Elution with 5% ethyl acetate in hexanes provided 110 mg (88%) of the title compound. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.51 (2H, m), 7.35 (3H, m), 6.12 (1H, dd, *J* = 18.8, 5.6 Hz), 5.95 (1H, dd, *J* = 18.8, 1.2 Hz), 3.88 (1H, t, *J* = 5.5 Hz), 1.6−1.8 (6H, m), 1.41 (1H, m), 1.1−1.3 (5H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 149.4, 134.3, 134.0, 129.1, 128.1, 127.9, 79.1, 43.4 , 28.8, 28.2, 26.1, 25.9, −2.7. IR (cm^{-1}, $CHCl_3$) 3400, 3362, 2925, 2852, 1619, 1450, 1427; 1373 1247, 1114, 1084, 842, 731, 700. HRMS *m/e* calcd for $C_{16}H_{33}OSi$: 274.1753. Found: 274.1733.

(Z)-1-Cyclohexyl-3-(dimethylphenylsilyl)prop-2-enol (24b). A mixture of 1-cyclohexyl-3-(dimethylphenylsilyl)prop-2-ynol (544 mg, 2.0 mmol), ^{t}BuMe$_2$SiCl (340 mg, 2.3 mmol), and imidazole (340 mg, 5.0 mmol) was stirred under nitrogen at room temperature for 48 h. The reaction mixture was then diluted with ether, washed with H_2O, and dried over $MgSO_4$. The *tert*-butyldimethylsilyl ether of 1-cyclohexyl-3-(dimethylphenylsilyl)prop-2-ynol was obtained as a colorless oil (703 mg, 91%) after column chromatography (10% ethyl acetate in hexanes). ^1H NMR (200 MHz, $CDCl_3$) δ: 7.66−7.61 (2H, m), 7.35−7.39 (3H, m), 4.13 (1H, d, *J* = 6.3 Hz), 1.92−0.92 (11H, m) 0.93 (9H, s), 0.42, 0.15, 0.12 (12H, 3s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 137.3, 133.9, 129.4, 127.9, 109.1, 87.0, 68.2, 44.6, 28.5, 28.5, 26.4, 25.9, 25.6, 25.7, 18.1, −1.1, −4.7, −5.3. IR (cm^{-1}, neat) 2955, 2926, 2855, 2171, 1251, 1087, 837. HRMS *m/e* calcd for $C_{23}H_{37}OSi_2$ ($M - H^+$): 385.2383. Found: 385.2384.

tert-Butyldimethylsilyl ether of 1-cyclohexyl-3-(dimethylphenylsilyl)prop-2-ynol (200 mg, 0.52 mmol) was dissolved in 3 mL of ether and the flask was cooled to −20 °C by a dry ice−carbon tetrachloride bath. DIBAL-H (neat, 0.11 mL, 0.5 mmol) was added to the flask at −20 °C and the mixture was heated to reflux for 2 h. After the mixture was cooled to 0 °C, 1.2 mL (2.5M in hexane, 3.0 mmol) of *n*-BuLi was added and the resulting yellowish solution was stirred at 0 °C for 10 min and room temperature for 50 min. The solvent was removed under vacuum and replaced with 3 mL of THF. After the resulting solution was cooled to −78 °C, small pieces of ice were added. The mixture was stirred at this temperature for 30 min and room temperature for 30 min to give a clear solution. The clear solution was then diluted with ether and washed with aqueous NH_4Cl, H_2O, and brine. The organic phase was dried over $MgSO_4$, and volatiles were removed under reduced pressure. The crude product was purified by column chromatography to yield 159 mg (80%) of *tert*-butyldimethylsilyl ether of (*Z*)-1-cyclohexyl-3-(dimethylphenylsilyl)prop-2-enol as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.50−7.56 (2H, m), 7.31−7.38 (3H, m,), 6.34 (1H, dd, *J* = 14.7, 8.7 Hz), 5.62 (1H, d, *J* = 14.7 Hz), 3.89(1H, dd, *J* = 8.7, 2.9 Hz), 1.78−1.50, 1.38−1.30, 1.23−0.81 (11H, m), 0.85 (9H, s), 0.396, 0.392, −0.082, −0.091 (12H, 4 s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 153.3, 139.3, 134.0, 129.2, 127.9, 126.1, 76.6, 45.4, 29.6, 26.7, 26.4, 26.2, 25.9, 25.7, 18.0), −1.00, −4.2, −5.0. IR (cm^{-1}, neat) 2955, 2927, 2854, 1250, 1101, 835. HRMS *m/e* calcd for $C_{23}H_{39}OSi_2$ ($M - H^+$): 387.2539. Found: 387.2528.

A mixture of *tert*-butyldimethylsilyl ether of (Z)-1-cyclohexyl-3-(dimethylphenylsilyl)prop-2-enol (80 mg, 0.21 mmol) and Dowex 50W-200 resin (1 g) in 2 mL of CH_3OH was stirred at room temperature for 15 h. The mixture was then filtered and the filtrate gave a pale yellow oil after removal of volatiles. Flash chromatography (silica gel, 10% ethyl acetate in hexanes) gave 42 mg (71%) of **24b** as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.53−7.50 (2H, m), 7.36−7.32 (3H, m), 6.34 (1H, dd, *J* = 14.4, 8.8 Hz), 5.84 (1H, d, *J* = 14.1 Hz), 3.80 (1H, t, *J* = 7.6 Hz), 1.80−1.45, 1.35−1.06, 0.90−0.71 (12H, m), 0.39 (3H, s), 0.38 (3H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 139.7, 130.5, 129.2, 128.1, 150.7, 133.8, 76.2, 43.4, 28.8, 28.2, 26.3, 26.0, 25.8, −0.9. IR (cm^{-1}, neat) 3404, 2932, 2856, 1255, 1112, 824. HRMS *m/e* calcd for $C_{16}H_{23}OSi$ ($M - CH_3^+$): 259.1518. Found: 259.1519.

(E)-1-Cyclohexyl-3-(dimethylphenylsilyl)but-2-enol (26). Following the general procedure for hydromagnesiation, ^{i}BuMgCl (0.25 mL, 0.49 mmol) Cp_2TiCl_2 (5.0 mg, 0.02 mmol) in 2 mL of ether was stirred for 15 min at 0 °C. A solution of 1-cyclohexyl-3-(dimethylphenylsilyl)prop-2-ynol (50 mg, 0.1945 mmol in 0.5 mL ether) was added via cannula to the Schlenk flask. After stirring at 0 °C for 10 min and warming to room temperature over 30 min, the solution was heated to reflux overnight. The ether was replaced with THF and the reaction mixture was cooled to 0 °C. Methyl iodide (0.1 mL, 0.23 mmol) was then added slowly with caution. After 1 h at 0 °C and 3 h at room temperature, the reaction mixture was extracted and purified by column chromatography. Elution with 5% ethyl acetate in hexanes provided 38 mg (68%) of the title compound. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.46 (2H, m), 7.33 (3H, m), 5.75(1H, dq, *J* = 3.5, 1.7 Hz), 4.23 (1H, t, *J* = 5.56 Hz), 1.90 (1H, d, *J* = 12.7 Hz) 1.68 (3H, d, *J* = 2.6 Hz), 0.8−2.0 (14H, m), 0.33 (6H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 142.3, 138.1, 137.4, 134.0, 129.0, 127.8, 72.0, 43.9, 28.6, 28.3, 26.4, 26.0, 25.8, 15.2, −3.8, −3.9. IR (cm^{-1}, $CHCl_3$) 3452, 2900, 1616, 1448, 1427; 1257, 1110, 836. HRMS *m/e* calcd for $C_{18}H_{28}OSi$ (M^+): 288.1909. Found: 288.1888.

(Z)-1-Cyclohexyl-3-(dimethylphenylsilyl)but-2-enol (27). A Schlenk flask was charged with the *tert*-butyldimethylsilyl ether of 1-cyclohexyl-3-(dimethylphenylsilyl)prop-2-ynol obtained as described in preparation of **24b** (180 mg, 0.47 mmol) and 3 mL of ether. The flask was cooled to −20 °C by a dry ice−carbon tetrachloride bath, DIBAL-H (neat, 0.11 m, 0.5 mmol) was added, and the mixture was stirred at −20 °C for 10 min. The resulting material was warmed to room temperature and then heated to reflux for 2 h. After the mixture

was cooled to 0 °C, 1.2 mL (2.5M in hexane, 3.0 mmol) of n-BuLi was added and the resulting yellowish solution was stirred at 0 °C for 10 min and room temperature for 50 min. The solvent was removed under vacuum and replaced with 2 mL of THF. After cooling the resulting solution to −78 °C, addition of a THF solution of CuI·P(OEt)$_3$ (36 mg, 0.1 mmol/2 mL) was followed by the addition of 1 mL of MeI (excess). The reaction mixture was then stirred at −78 °C for 20 min and room temperature for 48 h. The clear solution was then diluted with ether and washed with aqueous NH_4Cl, H_2O, and brine. The organic phase was dried over $MgSO_4$, and volatiles were removed under reduced pressure. The crude product was purified by column chromatography to yield 169 mg (90%) of (*Z*)-1-cyclohexyl-3-(dimethylphenylsilyl)but-2-enyl *tert*-butyldimethylsilyl ether as a colorless oil contaminated by 5% of (*Z*)-1-cyclohexyl-3-(dimethylphenylsilyl)prop-2-enyl *tert*-butyldimethylsilyl ether. The two compounds obtained above have same R_f value and separation was very difficult. A pure sample for characterization was obtained by chromatography on a small scale (silica gel, 0.5% ethyl acetate/99.5% pentane). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.46−7.53 (2H, m), 7.29−7.36 (3H, m), 6.03 (1H, dq, J = 8.9, 1.6 Hz), 3.90 (1H, dd, J = 8.8, 2.9 Hz), 1.77 (1H, d, J = 1.6 Hz) 1.76−1.54, 1.28−0.90 (11H, m), 0.84 (9H, s), 0.39 (3H, s), 0.41 (3H, s), −0.09, −0.11 (6H, 2s, tBuSi(CH_3)$_2$). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 148.1, 139.2, 134.1, 131.9, 129.1, 127.9, 75.2, 45.6, 29.7, 26.6, 26.5, 26.4, 26.2, 25.8, 24.8, 18.1, −1.5, −4.1, −4.8. IR (cm^{-1}, neat) 3068, 2953, 2928, 2854, 2361,1250, 834. HRMS *m/e* calcd for $C_{24}H_{42}OSi_2$ (M^+): 402.2774. Found: 402.2755.

The (*Z*)-1-cyclohexyl-3-(dimethylphenylsilyl)but-2-enyl *tert*-butyldimethylsilyl ether containing 5% of (*Z*)-1-cyclohexyl-3-(dimethylphenylsilyl)prop-2-enyl *tert*-butyldimethylsilyl ether (253 mg, 0.63 mmol) was dissolved in 5 mL of CH_3CN and cooled to 0 °C. A solution of HF in CH_3CN/H_2O (2 mL, 5%) was added and stirred for 10 min at 0 °C. The mixture was then allowed to warm and stirred at room temperature for another 5 h. The reaction mixture was diluted with ether, washed with saturated aqueous K_2CO_3 and brine, and dried over $MgSO_4$. Removal of solvent and column chromatography (silica gel, 5% ethyl acetate/95% hexane) provided 116 mg (64%) of the deprotected alcohols as a colorless oil. The title compound was separated from the protonated enol **24b** by preparative HPLC (C_{18}, 30% H_2O/70% CH_3CN). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.54−7.48 (2H, m), 7.36−7.31 (3H, m), 6.04 (1H, dq, J = 8.7, 1.6 Hz,), 3.75 (1H, dd, J = 9.8, 6.9 Hz), 1.85 (1H, d, J = 1.6 Hz) 1.76−1.40, 1.30−1.01, 0.95−0.61 (12H, 3m), 0.40 (3H, s), 0.41 (3H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 145.0, 139.6, 138.0, 133.8, 129.3, 128.1, 76.3, 43.6, 28.8, 28.4, 26.3, 26.0, 25.9, 25.1, −1.4. IR (cm^{-1}, neat) 3449, 2925, 2852, 1450, 1248, 1110, 815. HRMS *m/e* calcd for $C_{17}H_{25}OSi$ ($M - CH_3^+$): 273.1675. Found: 273.1669.

(*Z*)-4-(Triisopropylsilyl)oct-3-en-2-ol (30). t-BuLi (0.915 mL, 1.7 M in pentane, 1.56 mmol,) was added to a solution of the TIPS ether of (*Z*)-4-iodooct-3-en-2-ol (0.305 g, 0.74 mmol) in THF (7.5 mL) and the reaction stirred at −78 °C for 1 h. The mixture was warmed to room temperature, stirred for 1 h, and then quenched by addition of water. Extraction and purification gave **30** (166 mg, 79%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.01 (1H, dt, J = 9.8, 1.2 Hz), 4.36 (1H, m), 2.03 (2H, t, J = 6.9 Hz), 1.51−1.03 (29H, m), 0.88 (3H, t, J = 7.0 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 147.1, 138.4, 68.1, 37.5, 33.2, 24.1, 23.5, 19.9, 14.8, 13.5. IR (cm^{-1}, neat): 3385, 2918, 1455. HRMS *m/e* calcd for $C_{17}H_{36}OSi$ ($M - H^+$): 283.2457. Found: 283.2445.

(*E*)-4-(Dimethylphenylsilyl)pent-3-en-2-ol (32). Following the general procedure for hydromagnesiation, ^{i}BuMgCl (1.5 mL, 3.0 mmol) Cp_2TiCl_2 (38 mg, 0.15 mmol) in 2 mL of ether was stirred for 10 min at 0 °C. A solution of 4-(dimethylphenylsilyl)but-3-yn-2-ol (211 mg, 1.03 mmol) in 2 mL of ether was added via cannula to the Schlenk flask. After stirring at 0 °C for 10 min and warming to room temperature over 30 min, the solution was heated to reflux for 5 h. The ether was replaced with 3 mL of THF and the reaction mixture was cooled to 0 °C. Methyl iodide (1 mL, 2.3 mmol) was then added slowly with caution. After 1 h at 0 °C and overnight at room temperature, the reaction mixture was extracted and purified by column chromatography. Elution with 5% ethyl acetate in hexanes provided **32** (138 mg, 61% based on methylated product) contaminated with some protonated product. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.53−7.47 (2H, m), 7.47−7.32 (3H, m), 5.83 (1H, dq, J_1 = 7.8, J_2 = 1.7 Hz), 4.72 (1H, m), 1.71 (3H, d, J = 1.7 Hz) 1.25 (3H, d, J = 6.4 Hz), 0.37 (6H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 144.8 138.1, 134.1, 129.1, 127.9, 64.4, 22.9, 14.7, −3.9, −4.0.

(*Z*)-4-(Dimethylphenylsilyl)-4-(tributylstannyl)but-3-en-2-ol (36). Following the general procedure for hydromagnesiation, ^{i}BuMgCl (5.7 mL, 11.3 mmol) and Cp_2TiCl_2 (224 mg, 0.90 mmol) in 10 mL of ether was stirred for 10 min at 0 °C. A solution of 4-(dimethylphenylsilyl)but-3-yn-2-ol (922 mg, 4.5 mmol) in 2 mL of ether was added via cannula to the Schlenk flask. After stirring at 0 °C for 10 min and warming to room temperature over 30 min, the solution was heated to reflux for 4 h. The ether was replaced with THF (10 mL) and tributyltin chloride (3.0 mL, 11.1 mmol) was added. The reaction mixture was then heated to reflux for 3 h. The reaction mixture was extracted and purified by column chromatography. Elution with 10% ethyl acetate in hexanes provided **36** (1.12 g, 51%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.43−7.37 (2H, m), 7.37−7.24 (3H, m), 6.73(1H, d, J = 7.9, J_{Sn-H} = 161 Hz), 4.19−4.13 (1H, m), 1.58(1H, d, J = 3.2 Hz), 1.42−1.11, 0.91−0.55 (30H, 2m), 0.84 (3H, s), 0.81 (3H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 159.5 143.9, 139.0, 136.1, 128.7, 127.8, 73.5, 28.5, 27.1, 22.8, 13.2, 11.8, −2.0. ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −52.56. IR (cm^{-1}, neat): 3374, 2954, 1463.

(*Z*)-4-(Tributylstannyl)-4-(trimethylsilyl)but-3-en-2-ol (37). Following the general procedure, ^{i}BuMgCl (5.0 mL of 2.0 M solution in ether) and Cp_2TiCl_2 (100 mg) in 4.0 mL ether were stirred at 0 °C for 15 min. 4-(Trimethylsilyl)but-3-yn-2-ol (0.57 g, 4.0 mmol) in 2.0 mL of dry ether was added and the mixture heated to reflux overnight. The solvent was then removed *in vacuo* and 8.0 mL of dry THF added to dissolve the resulting solid. Tributyltin chloride (1.40 mL) was added and the resulting solution heated to reflux for 24 h.. Following workup and chromatography (10% ether in hexanes), **37** (1.26 g, 73%) was isolated. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.63 (1H, d, J = 7.8 Hz, J_{Sn-H} = 157.8 Hz, 4.08 (1H, m), 1.34 (16H, m), 0.89 (15H, m), 0.04 (9H, s). ^{13}C NMR (50 MHz, $CDCl_3$): δ 157.0, 144.2, 73.4, 29.5, 27.7, 23.2, 13.9, 12.0, 0.02. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −53.00. IR (cm^{-1}, neat): 3381, 2952, 2924, 2868, 2854, 1574, 1462, 1377, 1244, 1054, 892, 857, 836, 751. HRMS: calcd for $C_{18}H_{39}OSiSn$ ($M - CH_3^+$): 419.1792. Found: 419.1767. Calcd for $C_{15}H_{33}OSiSn$ ($M - C_4H_9^+$): 377.1323. Found: 377.1310.

(*Z*)-1-Methoxy-4-(tributylstannyl)-4-(trimethylsilyl)-but-3-en-2-ol (38). Following the general procedure, ^{i}BuMgCl (1.1 mL, 2.2 mmol) and Cp_2TiCl_2 (25 mg, 0.099 mmol) in 5 mL of ether was stirred for 10 min at 0 °C. A solution of the propargyl alcohol (172 mg, 1.0 mmol) in 2 mL of ether was added via cannula to the Schlenk flask. After stirring at 0 °C for 10 min and warming to room temperature, the solution was heated to reflux for 5 h. The ether was replaced with THF and $ClSnBu_3$ (0.5 mL, 1.84 mmol) was added. After 2 h at reflux and cooling to room temperature, the reaction mixture was extracted and purified by column chromatography. Elution with 5% ethyl acetate in hexanes provided **38** (363 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.57 (1H, d, J = 7.4, $J_{SnC=CH}$ = 164.9 Hz), 4.13 (1H, m), 3.38 (3H, s), 3.37−3.28 (2H, m), 2.41 (1H, d, J = 2.2 Hz), 1.46−0.83 (27H, m), 0.038 (9H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 151.3, 149.5, 76.2, 75.1, 58.9, 29.0, 27.3, 13.4, 11.6, −0.6. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −51.95. IR (cm^{-1}, neat) 3454−3348, 2954, 2924, 1463, 1245, 1073, 832. HRMS *m/e* calcd for $C_{16}H_{35}O_2SnSi$ ($M - C_4H_9^+$): 407.1428. Found: 407.1437.

(*Z*)-6-(Tributylstannyl)-6-(trimethylsilyl)hex-5-en-4-ol (39). As in the general procedure, Cp_2TiCl_2 (33.4 mg , 0.14 mmol) was dissolved in ether (3 mL) and cooled to 0 °C, and then ^{i}BuMgCl (1 mL, 2.0 M in diethyl ether, 2 mmol) was added. The alcohol (152.7 mg, 0.90 mmol) was added and the mixture was heated to reflux. After 5 h, the solvent was removed and the solid redissolved in THF (3 mL). Tributyltin chloride was added (0.3 mL, 1.1 mmol) and the mixture heated to reflux for 2 h. Workup and flash chromatography yielded

39 (238.9 mg, 58%) (unoptimized yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 6.63 (1H, d, J = 7.8 Hz), 3.88 (1H, m,), 1.52–1.20 (17H, m), 0.94–0.827 (18H, m), 0.04 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.5, 146.0, 76.8, 39.0, 29.2, 27.4, 18.8, 14.2, 13.6, 11.7, −0.3. ^{119}Sn NMR (112 MHz, $CDCl_3$) δ: −54.05; IR (cm^{-1}, neat) 3487, 2959, 2924, 2875, 2868, 1574, 1462, 1377, 1244, 1068, 878, 835. HRMS: calcd for $C_{21}H_{45}OSiSn$ (M − H)$^+$ 441.2262. Found 461.2268. Calcd for $C_{20}H_{43}OSiSn$ (M − CH_3^+): 447.2105. Found: 447.2120. Calcd for $C_{17}H_{37}OSiSn$ (M − $C_4H_9^+$): 405.1636. Found: 405.1622.

(*Z*)-4-(Triisopropylsilyl)-4-(trimethylsilyl)but-3-en-2-ol (42). (*Z*)-4-(Tributylstannyl)-4-(trimethylsilyl)but-3-en-2-ol (**37**) (500 mg, 1.15 mmol) dry THF, (0.5 mL) and freshly distilled triethylamine (0.40 mL, 0.29 g, 2.87 mmol, 2.5 equiv) were added to a flame-dried flask, followed by freshly distilled chlorotrimethylsilane (0.220 mL, 0.188 g, 1.73 mmol, 1.5 equiv). The mixture was stirred for 0.5 h and then passed through a small plug of silica gel and rinsed with ether to give the crude product, which was further purified by flash chromatography on a silica gel column (5% ether in hexanes) yielding (540 mg, 93%) of pure product which was carried immediately on to the next step. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.74 (1H, d, J = 6.6 Hz; J_{Sn-H} = 173 Hz), 4.17 (1H, dq, J = 6.6, 6.3 Hz), 1.58–1.20 (12H, m), 1.19 (3H, d, J = 6.3 Hz), 1.02 (21H, m), 0.95–0.80 (15H, m), 0.04 (9H, s). ^{13}C NMR (50 MHz, $CDCl_3$): δ 161.8, 138.6, 73.8, 29.3, 27.5, 25.2, 18.1 (2), 13.6, 12.4, 11.4, 0.03. IR (cm^{-1}, neat): 2959, 2938, 2868, 1574, 1461, 1244, 1089, 1068, 1005, 871, 836. HRMS: calcd for $C_{24}H_{53}OSi_2Sn$ (M − $C_4H_9^+$): 533.2657. Found: 533.2647.

The silyl ether (0.335 g, 0.568 mmol) in THF (1.4 mL) was added via cannula to a solution of MeLi (0.50 mL, 1.37 M in ether, 0.685 mmol) in THF (1.6 mL) and the reaction stirred at −78 °C for 2 h before being allowed to warm to room temperature. Following quenching the reaction with water and extraction, purification by flash chromatography on silica gel (hexanes:diethyl ether 20:1) gave the title compound as a clear oil (160 mg, 94%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 6.65 (1H, d, J = 9.2 Hz), 4.38 (1H, ddq, J = 9.2, 6.1, 3.3 Hz), 1.35 (1H, d, J = 3.3 Hz), 1.20 (3H, d, J = 6.1 Hz), 1.05 (18H, m), 0.13 (9H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 162.2, 138.4, 69.4, 22.5, 19.3, 13.5, 1.7. IR (cm^{-1}, neat): 3423, 2959, 2924, 2875, 2853, 1574, 1461, 1377, 1243, 1075, 1046. HRMS: calcd for $C_{15}H_{33}OSi_2$ (M − CH_3^+): 285.2084. Found: 285.2070. Calcd for $C_{13}H_{29}OSi_2$ (M − C_3H_7)$^+$ 257.1755. Found: 257.1757.

(*E*)-4-(Tributylstannyl)-4-(triisopropylsilyl)but-3-en-2-ol (43). A mixture of 4,4-bis(tributylstannyl)but-3-en-2-ol (**44**) (171 mg, 0.26 mmol), ^{i}Pr$_3$SiCl (90 mg, 0.47 mmol), and imidazole (60 mg, 0.88 mmol) in 1 mL of DMF was stirred under nitrogen at room temperature for 48 h. The reaction mixture was then diluted with ether, washed with H_2O, and dried over $MgSO_4$. The triisopropylsilyl ether of 4,4-bis-(tributylstannyl)but-3-en-2-ol was obtained as a colorless oil (205 mg, 98%) after column chromatography (10% ethyl acetate in hexanes). ^{1}H NMR (200 MHz, $CDCl_3$) δ : 6.70 (1H, d, J = 6.8 Hz, $^3J_{SnC-CH}$ = 189.4, 103.3 Hz), 4.08 (1H, m), 1.56–0.74 (78H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ : 164.4, 138.3, 74.9, 25.5, 29.2, 29.0, 27.5, 27.4, 13.5, 13.4, 11.2, 10.3, 17.9, 12.2. IR (cm^{-1}, neat) 2958, 2926, 28.68, 1463, 1376, 1087.

Methyllithium (2.4 mL, 1.4 M in Et_2O, 3.36 mmol) was added to a solution of the TIPS protected alcohol of **44** (190 mg, 0.24 mmol) in 2.5 mL of THF at 0 °C. After 2.5 h stirring at 0 °C, the mixture was warmed to rt for 1.5 h. The reaction mixture was then treated with water and extracted with ether. The ether layer was washed with brine and dried over $MgSO_4$. Flash chromatography (10% ethyl acetate in hexanes, SiO_2) gave **43** (49 mg, 40%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 6.53 (1H, d, J = 8.9 Hz, $J_{SnC=CH}$ = 109.4 Hz), 4.24 (1H, m), 1.23 (3H, d, J = 6.1 Hz), 1.54–0.79 (49H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 162.5, 141.5, 70.5, 22.7, 28.9, 27.3, 13.8, 13.5, 19.0, 11.7. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −20.08. IR (cm^{-1}, neat) 3405, 2955, 2925, 28.67, 1463, 1376, 1071, 881. HRMS *m/e* calcd for $C_{25}H_{54}OSiSn$ (M$^+$): 518.2949. Found: 518.2966.

4,4-Bis(tributylstannyl)but-3-en-2-ol (44). Following the general procedure, ^{i}BuMgCl (3.0 mL, 6.0 mmol) and Cp_2TiCl_2 (80 mg, 0.35 mmol) in 10 mL of ether was stirred for 10 min at 0 °C. A solution of the (tributylstannyl)propargyl alcohol[32] (716 mg, 2.0 mmol) in 4 mL ether was added via cannula to the Schlenk flask. After stirring at 0 °C for 10 min and warming to room temperature, the solution was heated to reflux for 4 h. The ether was replaced with THF, and $ClSnBu_3$ (1.0 mL, 3.7 mmol) was added. After 2 h at reflux and overnight at room temperature, the reaction mixture was extracted and purified by column chromatography. Elution with 10% ethyl acetate in hexanes provided **44** (678 mg, 53%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 6.62 (1H, d, J = 7.5 Hz, J_{SnC-CH} = 176.6, 98.3 Hz), 3.97 (1H, m), 2.15 (1H, s), 1.25 (3H, d, J = 6.2 Hz), 1.56–0.81 (54H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 160.6, 145.0, 74.4, 22.8, 29.2, 29.0, 27.4, 27.3, 13.465 11.5, 10.1. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −22.60, −48.36. IR (cm^{-1}, neat) 3422–3373, 2957, 2925, 1463, 1376, 1070. HRMS *m/e* calcd for $C_{24}H_{51}OSn_2$ (M − $C_4H_9^+$): 595.1984. Found: 595.1955.

4,4-Bis(trimethylsilyl)but-3-en-2-ol (45). A solution of (*Z*)-4-(tributylstannyl)-4-(trimethylsilyl)but-3-en-2-ol trimethylsilyl ether (0.75 g, 1.48 mmol) in THF (3.5 mL) was added via cannula to a solution of MeLi (1.30 mL, 1.37 M in ether, 1.78 mmol) in THF (4.0 mL) at −78 °C. The mixture was stirred for 2 h before being allowed to warm to room temperature, quenched, extracted, and purified as indicated above to give two major products; **45** (186 mg, 58%) and (*Z*)-4-(tributylstannyl)-4-trimethylsilylbut-3-en-2-ol (37%); i.e. to have resulted from cleavage of the Si—O bond rather than the C—Sn bond. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.45 (1H, d, J = 8.7 Hz), 4.53 (1H, m), 1.55 (1H, s), 1.21 (3H, d, J = 6.1 Hz), 0.15 (9H, s), 0.07 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.4, 142.6, 69.4, 23.0, 2.3, 0.3. IR (cm^{-1}, neat) 3337, 2959, 1581, 1248, 1057, 839. HRMS *m/e* calcd for $C_{10}H_{23}OSi_2$ (M − H$^+$): 215.1287. Found: 215.1288.

General Procedure for the Homogeneous Hydrogenation of Vinyl Stannanes and Silanes. The hydrogenation bomb (part no. 4712 screw cap bomb) and gauge block assembly (no. 4316) were obtained from Parr Instrument Co. A glass sleeve was used to line the interior of the bomb. The substrate, 5–20 mol % of the rhodium catalyst, and a stirbar were added to the flame-dried sleeve. Dry, distilled, deaerated dichloromethane was added to the mixture to make a 0.10–0.25 M solution. The sleeve was quickly transferred into the bomb which had also been flushed with nitrogen, and the gauge block assembly was attached. The nuts were tightened and the system pressurized to 200 psi with ultrahigh purity hydrogen gas. The pressure was released and the system was flushed three times. The nuts were tightened once more and the pressure was increased to 1400–1500 psi with stirring for 24–48 h. After this time, the pressure was released at the hose and the catalyst residue was precipitated by the addition of hexane. The suspension was filtered through Na_2SO_4 or a small amount of silica gel and the volatiles removed *in vacuo*. The hydrogenated product was obtained as an oil and flash chromatography on silica gel was used for purification when necessary.

1-Cyclohexyl-3-(tributylstannyl)propanol (9). The dried sleeve was charged with **7** (100 mg 0.23 mmol) and 8 mg (0.011 mmol, 5 mol %) of the catalyst. Dichloromethane (1.0 mL) was added and the hydrogenation was carried out at 1500 psi. After 39 h, the catalyst was removed and the product purified by flash chromatography (5% ethyl acetate in hexanes as eluent) to yield 67 mg (67%) of the hydrogenated product along with 16.9 mg (17%) of recovered **7**. ^{1}H NMR (400 MHz, $CDCl_3$) δSPCLN 3.20 (1H, m), 1.58–1.80 (6H, m), 1.54 (4H, m), 1.44 (6H, m), 1.28 (6H, m), 0.97–1.20 (4H, m), 0.87 (t, 9H, J = 7.20 Hz), 0.80 (6H, m), 0.66 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δSPCLN 79.1, 42.7, 30.9, 29.2, 27.4, 29.5, 27.6, 26.6, 26.4, 26.2, 13.7, 8.8, 4.0. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −7.3. IR (cm^{-1}, $CHCl_3$) 3370, 2950, 1463, 1450, 1376, 1079. HRMS *m/e* calcd for $C_{17}H_{35}OSn$ (M − $C_4H_9^+$): 375.1710. Found: 375.1721.

3-(Tributylstannyl)butanol (10). The dried sleeve was charged with **8** (28 mg, 0.079 mmol) and 10 mg (0.014 mmol,

(32) Prepared by addition of the lithium anion of (tributylethynyl)-stannane to acetaldehyde, see: Renaldo, A. F.; Labadie, J. W.; Stille, J. K. *Org. Synth.* **1989**, *67*, 89.

ca. 17 mol %) of the catalyst. Dichloromethane (0.5 mL) was added and the hydrogenation carried out at 1400 psi. After 36 h, the catalyst was removed and the product purified by flash chromatography (5% ethyl acetate in hexanes as eluent) to yield 17 mg (59%) of the hydrogenated product. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.64 (1H, t, J = 5.3 Hz), 1.55 (5H, m), 1.45 (6H, m) and 1.27 (8H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δSPCLN 62.6, 54.7, 37.4, 29.1, 27.2, 23.0, 13.5, 8.5. IR (cm^{-1}, $CHCl_3$) 3365, 3630, 1551, 1458, 1376, 1070. HRMS *m/e* calcd for $C_{21}H_{43}OSn$ ($M - C_4H_9^+$): 431.2335. Found: 431.2337.

(*1S*,3S)-1-Cyclohexyl-3-(tributylstannyl)heptanol (12).** The dried sleeve was charged with **11** (224 mg, 0.44 mmoles) and 17 mg (0.022 mmol, 5 mol %) of catalyst. Dichloromethane (2 mL) was added and the hydrogenation carried out at 1500 psi. After 25 h, the catalyst was removed and the product purified by flash chromatography (5% ethyl acetate in hexanes as eluent) to yield 190 mg (85%) of the hydrogenation product along with 2.9 mg (3%) of hydrogenolysis product, **13**. In another experiment, 40.5 mg (0.08 mmol) of **11** and 10 mg (0.014 mmol, 17 mol %) of catalyst in 0.5 mL of dichloromethane gave 28 mg (70%) of **12** and 2.2 mg (13%) of **13**. ^{1}H NMR (400 MHz, $CDCl_3$) δSPCLN 3.4 (1H, brs), 1.56−1.8 (8H, m), 1.55 (4H, m), 1.4−1.45 (7H, m), 0.98−1.3 (17H, m), 0.87, (9H, t, J = 7.29 Hz), 0.79 (6H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 74.3, 43.8, 37.3, 32.3, 32.1, 29.3, 26.4, 26.3, 26.1, 29.2, 27.4, 22.9, 22.2, 13.9, 13.5, 8.8. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δSPCLN −10.58. IR (cm^{-1}, neat) 3631, 2926, 1464, 1457, 1451, 1376, 1101. MS *m/e* calcd for $C_{21}H_{43}OSn$ ($M - C_4H_9^+$): 431.2335. Found: 431.2337. Anal. Calcd for $C_{25}H_{52}OSn$: C, 61.61; H, 10.75. Found: C, 61.90; H, 10.37.

(*1S*,3R)-1-Cyclohexyl-3-(tributylstannyl)-4-methylpentanol (15).** The dried sleeve was charged with **14** (104 mg, 0.22 mmol) and 8 mg (0.011 mmol, 5 mol %) of the catalyst. Dichloromethane (2 mL) was added and the hydrogenation carried out at 1500 psi. After 48 h, the catalyst was removed and the product purified by flash chromatography (5% ethyl acetate in hexanes as eluent) to yield 87 mg (83%) of the hydrogenated product. ^{1}H NMR (400 MHz, $CDCl_3$) δSPCLN 3.37 (1H, m), 2.05 (1H, m), 1.75 (2H, m), 1.65 (2H, m) and 1.54 (2H, m), 1.45 (7H, m), 1.29 (6H, m), 1.23 (6H, s,), 1.2−0.9 (6H, m), 0.87 (12H, m), 0.80 (6H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δSPCLN 74.7, 43.6, 34.6, 32.6, 29.6, 29.3, 29.2, 27.3, 26.4, 26.3, 26.1 27.5, 21.9, 13.5, 9.8. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δSPCLN −14.6. IR (cm^{-1}, $CHCl_3$), 3621, 2855, 2933, 1550; 1464, 1459, 1451, 1377, 1360, 1100. HRMS *m/e* calcd for $C_{20}H_{41}OSn$ ($M - C_4H_9^+$): 417.2179. Found: 417.2189. Anal. Calcd for $C_{24}H_{50}OSn$: C, 60.90; H, 10.65. Found: C, 61.68; H, 10.72.

(*1S*,3R)-1-Cyclohexyl-3-(tributylstannyl)-4,4-dimethylpentan-ol (17).** The dried sleeve was charged with **16** (64 mg, 0.12 mmol) and 15 mg (0.021 mmol, 17 mol %) of the catalyst. Dichloromethane (0.5 mL) was added and the hydrogenation carried out at 1400 psi. After 36 h, the catalyst was removed and the product purified by flash chromatography (5% ethyl acetate in hexanes as eluent) to yield 45 mg (70%) of the hydrogenated product. ^{1}H NMR (400 MHz, $CDCl_3$) δSPCLN 3.33 (1H, m), 1.88 (1H, m), 1.58−1.80 (6H, m), 1.55 (4H, m), 1.40−1.52 (6H, m), 1.30 (6H, m), 1.23 (1H, s), 1.0−1.2 (4H, m), 0.91 (9H, s), 0.87 (9H, t, J = 7.26 Hz), 0.82 (6H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δSPCLN 77.4, 42.6, 39.1, 34.7, 34.1, 30.7, 29.8, 29.6, 26.4, 26.2, 26.1, 29.2, 27.5, 13.5, 10.8. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δSPCLN −12.7. IR (cm^{-1}, $CHCl_3$) 3618, 2930, 1455, 1450, 1376, 1071. HRMS *m/e* calcd for $C_{21}H_{43}OSn$ ($M - C_4H_9^+$): 431.2336. Found: 431.2337. Anal. Calcd for $C_{25}H_{52}OSn$: C, 61.61; H, 10.75. Found: C, 61.99; H, 10.67.

(*1R*,3S)-3-(Tributylstannyl)octan-2-ol (19).** The dried sleeve was charged with **18** (84 mg, 0.20 mmol) and 8 mg (0.011 mmol, 5 mol %) of the catalyst. Dichloromethane (1 mL) was added and the hydrogenation carried out at 1500 psi. After 46 h, the catalyst was precipitated by the addition of hexanes and filtered through Na_2SO_4. After removal of volatiles, the residual oil was redissolved in ether and filtered through silica gel to yield 80 mg (95%) of the hydrogenated product. ^{1}H NMR (400 MHz, $CDCl_3$) δSPCLN 3.83 (1H, m), 1.62 (3H, m), 1.50−1.59 (2H, m), 1.40−1.45 (8H, m), 1.29 (12H m), 1.16 (3H, d, J = 6.04 Hz), 0.87 (9H, t, J = 7.26 Hz), 0.80 (6H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δSPCLN 66.7, 42.9, 32.4, 32.3, 29.2, 27.4, 23.7, 22.9, 22.5, 13.9, 13.5, 8.7. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δSPCLN −10.59. IR (cm^{-1}, neat) 3473, 2958, 1463, 1451, 1376, 1070, 592. HRMS *m/e* calcd for $C_{16}H_{35}OSn$ ($M - C_4H_9^+$): 363.1710. Found: 363.1697.

Reductive Destannation of (*Z*)-1-Cyclohexyl-3-(tributylstannyl)hept-2-enol (20). The dried sleeve was charged with **20** (32 mg, 0.066 mmol) and 10 mg (0.014 mmoles, 20 mol %) of catalyst. Dichloromethane (1 mL) was added and the hydrogenation carried out at 1500 psi. After 48 h, the catalyst was removed and the oily material was purified by flash chromatography (5% ethyl acetate in hexanes as eluent) to yield 6 mg (45%) of the hydrogenolysis product: **13** as indicated by ^{1}H NMR along with 6 mg (20%) of **20**. When the same reaction was carried out with 5 mol % of catalyst under 1400 psi of hydrogen, **13** was obtained in 20% yield and 80% of the starting material was recovered. The hydrogenation product was not detected in these reactions. ^{1}H NMR (400 MHz, $CDCl_3$) δSPCLN 3.33 (1H, m), 1.76 (2H, m), 1.64 (2H, m), 1.55 (1H, s), 1.5−0.9 (16H, m), 0.86 (3H, m).

(2*R,4*R**)-3-(Tributylstannyl)octan-2-ol (22).** The dried sleeve was charged with **21** (70 mg, 0.17 mmol) and 25 mg (0.035 mmol, 20 mol %) of the catalyst. Dichloromethane (1 mL) was added and hydrogenation carried out at 1500 psi. After 48 h, the catalyst was precipitated by the addition of hexane and filtered through Na_2SO_4. After removal of volatiles, the residue was redissolved in ether and filtered through silica gel. The product was purified by flash chromatography (5% ethyl acetate in hexanes as eluent) to yield 36 mg (51%) of **23**. ^{1}H NMR (200 MHz, $CDCl_3$) δSPCLN 3.80−3.75 (1H, m), 1.79−1.10, 1.02−0.65 (40H, 2m), 1.16 (3H, d, J = 6.1 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δSPCLN 67.8, 43.0, 33.0, 32.2, 29.2, 27.4, 23.5, 22.8, 23.3, 13.9, 13.4, 8.8. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −12.16. IR (cm^{-1}, neat) 3346, 2966, 1468, 1377, 1075. HRMS *m/e* calcd for $C_{16}H_{35}OSn$ ($M - C_4H_9^+$): 363.1710. Found: 363.1716.

Hydrogenation of (*E*)-1-Cyclohexyl-3-(dimethylphenylsilyl)prop-2-enol (24a). The dried sleeve was charged with **24a** (69 mg 0.25 mmol) and 10 mg (0.014 mmol, 5 mol %) of the catalyst. Dichloromethane (1 mL) was added and hydrogenation was carried out at 1400 psi. After 44 h, the catalyst was removed by filtration through Na_2SO_4 to yield 69 mg (99%) of **25**. ^{1}H NMR (400 MHz, $CDCl_3$) δSPCLN 7.4−7.6 (2H, m), 7.3−7.4 (3H, m), 3.23 (1H, m), 1.56−1.8 (5H, m), 0.88−1.55 (11H, m), 0.65 (1H, ddd, J = 14.3, 12.5, 4.6 Hz), 0.26 (6H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δSPCLN 139.2, 133.5, 128.9, 127.8, 78.3, 42.7, 29.4, 28.1, 27.6, 26.5, 26.4, 26.2, 11.2, −3.09, −3.13. IR (cm^{-1}, $CHCl_3$) 3630, 3070, 2942, 2634, 1554, 1546, 1450, 1378, 1252, 1114, 1094, 834, 724. HRMS *m/e* calcd for $C_{16}H_{25}OSi$ ($M-CH_3^+$): 261.1675. Found: 261.1673. Anal. Calcd for $C_{17}H_{28}OSi$: C, 73.85; H, 10.20. Found: C, 73.94; H, 10.16.

Hydrogenation of (*Z*)-1-Cyclohexyl-3-(dimethylphenylsilyl)prop-2-enol (24b). The dried sleeve was charged with **24b** (42 mg 0.17 mmol) and 19 mg (0.027 mmol, 16 mol %) of the catalyst. Dichloromethane (1 mL) was added and hydrogenation carried out at 1400 psi. After 42 h, the catalyst was removed by filtration through Na_2SO_4 to yield 38 mg (90%) of the hydrogenated product. The ^{1}H and ^{13}C NMR spectra of the product are identical to those of the **25** obtained from **24a**.

(*1S*,3S)-1-Cyclohexyl-3-(dimethylphenylsilyl)butanol (28).** The dried sleeve was charged with **26** (72 mg 0.25 mmol) and 10 mg (0.014 mmol, 5 mol %) of the catalyst. Dichloromethane (1 mL) was added and hydrogenation carried out at 1400 psi. After 48 h, the catalyst was removed by filtration through Na_2SO_4 to yield 71.5 mg (99%) of the hydrogenated product. ^{1}H NMR (400 MHz, $CDCl_3$) δSPCLN 7.47−7.51 (2H, m), 7.31−7.35 (3H, m), 3.4 (1H, ddd, J = 10.3, 5.7, 2.2 Hz), 1.54−1.82 (5H, m), 1.44 (1H, ddd, J = 13.5, 10.4, 2.2 Hz), 1.90−1.26 (8H, m), 0.96 (1H, m), 0.90 (3H, d, J = 7.0 Hz), 0.244 (3H, s), 0.240 (3H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.5, 134.1, 129.0, 127.8, 72.9, 44.1, 35.5, 29.1, 28.0, 26.4, 26.2, 26.0, 14.3, 13.2, −5.3, −5.4. IR (cm^{-1}, neat) 3373, 2929, 1450, 1427, 1327, 1112, 835, 813, 769, 734, 700. HRMS *m/e* calcd for $C_{17}H_{27}OSi$ ($M - CH_3^+$): 275.1831. Found: 275.1847.

Anal. Calcd for $C_{18}H_{30}OSi$: C, 74.48; H, 10.41. Found: C, 74.77; H, 10.57.

(1S*,3R*)-1-Cyclohexyl-3-(dimethylphenylsilyl)butanol (29). The dried sleeve was charged with **27** (30 mg, 0.10 mmol) and 15 mg (0.021 mmol, 20 mol %) of the catalyst. Dichloromethane (1 mL) was added and hydrogenation carried out at 1400 psi. After 48 h, the catalyst was removed by filtration through Na_2SO_4 to yield 28.5 mg (95%) of the hydrogenated product. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.47–7.50 (2H, m), 7.31–7.35 (3H, m), 3.37 (1H, td, J = 6.8, 3.7 Hz), 1.73–1.59 (4H, m) 1.56–1.49 (2H, 2m), 1.30–1.11 (8H, m), 0.99 (1H, m), 0.96–84 (1H, m), 0.261 (3H, s), 0.253 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.5, 133.9, 128.9, 127.7, 75.4, 42.3, 36.8, 29.8, 26.6, 26.5, 26.2, 26.2, 16.5, 15.4, −4.6, −5.2. IR (cm^{-1}, neat) 3382, 2954, 2925, 2859, 1258. HRMS m/e calcd for $C_{17}H_{27}OSi$ (M − CH_3^+): 275.1831. Found: 275.1838.

(2R*,4R*)-4-(Triisopropylsilyl)octan-2-ol (31). (Z)-4-(Triisopropylsilyl)oct-3-en-2-ol (25.9 mg, 0.13 mmol) was placed in the flame-dried glass sleeve as indicated in the general procedure, followed by 5.2 mg (6 mol %) of the rhodium(I) catalyst and 0.50 mL of deoxygenated dichloromethane. The hydrogenation was carried out at 1500 psi for 16 h and the product purified to give **31** (24.3 mg, 93%). ^1H NMR (200 MHz, $CHCl_3$): δ 3.8–4.0 (1H, m), 1.61 (4H, m), 1.54–0.95 (26H, m), 0.85 (7H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 68.2, 42.2, 33.9, 31.7, 23.3, 22.8, 19.6, 19.2, 14.1, 11.3. IR (cm^{-1}, neat) 3373, 2929, 1450, 1427, 1327, 1112, 835, 813, 769, 734, 700. HRMS m/e calcd for $C_{17}H_{37}OSi$ (M − H^+): 285.2614. Found: 285.2600.

(2R*,4S*)-4-(Dimethylphenylsilyl)pentan-2-ol (33). The dried sleeve was charged with **32** (110 mg, contaminated with 4-(dimethylphenylsilyl)but-3-en-2-ol, i.e. the protonated product from the Sato reaction) and 20 mg (0.028 mmol, 5.5 mol %) of the catalyst. Dichloromethane (1 mL) was added and the pressure of hydrogenation was increased to 1500 psi. After 25 h, the catalyst was removed by filtration through Na_2SO_4 to yield 105 mg (95%) of the hydrogenated products. For **33**, ^1H NMR (200 MHz, $CDCl_3$) δ: 7.52–7.49 (2H, m), 7.37–7.34 (3H, m), 3.87 (1H, m), 1.49, 1.16 (4H, m), 1.14 (3H, d, J = 6.1 Hz), 0.96 (3H, d, J = 6.9 Hz), 0.273 (3H, s), 0.269 (3H, s). It was not possible to separate the 3-(dimethylphenylsilyl)butan-2-ol; therefore, no further characterization was obtained.

Reductive Destannation of (Z)-1-Cyclohexyl-3-(tributylstannyl)-3-(dimethylphenylsilyl)prop-2-enol (41). The dried sleeve was charged with **41** (100 mg 0.18 mmol) and 7 mg (0.01 mmol, 5 mol %) of the catalyst. Dichloromethane (1 mL) was added and hydrogenation carried out at 1500 psi. After 24 h, the catalyst was removed by filtration through Na_2SO_4. After removal of volatiles, the product was purified by flash chromatography (5% ethyl acetate in hexane as eluent) to yield 9 mg (18%) of **25** as a colorless oil along with 85 mg (85%) of unreacted **41**. The ^1H and ^{13}C NMR spectra of the product are identical to that of **25** obtained from **24a**.

3-(Tributylstannyl)-3-(trimethylsilyl)propanol (46). The dried sleeve was charged with **35** (200 mg, 0.42 mmol) and 15 mg (0.021 mmol, 5 mol %) of the catalyst. Dichloromethane (1 mL) was added and the hydrogenation carried out at 1500 psi. After 15 h, the catalyst was precipitated by the addition of hexanes and filtered through Na_2SO_4. After removal of volatiles, the product was purified by flash chromatography (5% ethyl acetate in hexanes) to yield **46** (198 mg, 99%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.62–3.43 (2H, m), 1.95–1.70, 1.53–1.22, 1.02–0.76 (30H, 3m), 0.22 (1H, dd, J = 7.7, 6.5 Hz), −0.015 (9H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 65.6, 31.5, 29.2, 27.4, 13.5, 10.0, 6.3, −0.1. ^{119}Sn NMR (74.5 MHz, $CDCl_3$), δ: −0.13. IR (cm^{-1}, neat) 3297, 2966, 2931, 2853, 1457, 1250, 1025, 850. HRMS m/e calcd for $C_{14}H_{33}OSiSn$ (M − $C_4H_9^+$): 365.1323. Found: 365.1327.

(2R*,4S*)-4-(Tributylstannyl)-4-(dimethylphenylsilyl)-butan-2-ol (47). The dried sleeve was charged with **36** (247 mg, 0.50 mmol) and 20 mg (0.028 mmol, 5.6 mol %) of the catalyst. Dichloromethane (1 mL) was added and the hydrogenation carried out at 1500 psi. After 24 h, the catalyst was precipitated by the addition of hexanes and filtered through Na_2SO_4. After removal of volatiles, the residue was redissolved in ether and filtered through silica gel to yield **47** (235 mg, 95%). ^1H NMR (200 MHz, $CDCl_3$) δ: 7.52–7.46, 7.33–7.30 (5H, 2m), 3.65–3.45 (1H, m), 1.77–1.50 (2H, m), 1.45–1.08, 0.8–0.65 (29H, 2m), 1.09 (3H, d, J = 6.1 Hz), 0.28 (3H, s), 0.26 (3H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 140.7, 133.7, 128.9, 127.9, 69.9, 37.9, 29.0, 27.4, 13.4, 10.0, 23.4, 6.4, −1.5, −2.1. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −0.01. IR (cm^{-1}, neat) 3422, 2957, 1462, 1247, 1110, 831. HRMS m/e calcd for $C_{20}H_{37}OSiSn$ (M − $C_4H_9^+$): 441.1636. Found: 441.1621.

(2R*,4S*)-4-(Tributylstannyl)-4-(trimethylsilyl)butan-2-ol (48). (Z)-4-(Tributylstannyl)-4-(trimethylsilyl)but-3-en-2-ol (**37**) (23.4 mg, 0.054 mmol) was placed in the flame-dried glass sleeve as indicated in the general procedure, followed by 1.9 mg (5 mol %) of the rhodium(I) catalyst and 0.50 mL of deoxygenated dichloromethane. The hydrogenation was carried out at 1500 psi for 16 h and the product purified to give **48** (22.9 mg, 96%). ^1H NMR (200 MHz, $CDCl_3$): δ 3.65 (1H, m), 1.70 (2H, m), 1.36 (13H, m), 1.17 (3H, d, J = 6.1 Hz), 0.842 (15H, m), 0.39 (1H, dd, J = 9.0, 6.1 Hz), −0.01 (9H, s). ^{13}C NMR (50 MHz, $CDCl_3$): δ 70.0, 38,1, 29.3, 27.6, 23.5, 13.7, 10.2, 7.6, 0.06. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −2.62. HRMS: Calcd for $C_{18}H_{41}OSiSn$ (M − CH_{3+}): 421.1949. Found: 421.1924. Calcd for $C_{15}H_{35}OSiSn$ (M − C_4H_{9+}): 379.1479. Found: 379.1484.

(2S*,4S*)-1-Methoxy-4-(tributylstannyl)-4-(trimethylsilyl)butan-2-ol (49). The dried sleeve was charged with **38** (231 mg, 0.50 mmoles) and 50 mg (0.071 mmol, 15 mol %) of the catalyst. Dichloromethane (1 mL) was added and the hydrogenation was carried out at 1500 psi. After 48 h, the catalyst was precipitated by the addition of hexanes and filtered through Na_2SO_4. After removal of volatiles, the product was purified by flash chromatography (5% ethyl acetate in hexanes) to yield **49** (208 mg, 90%). ^1H NMR (200 MHz, $CDCl_3$) δ: 3.71–3.60 (1H, m), 3.39 (1H, AB, J = 9.4, 3.0 Hz), 3.17 (1H, AB, J = 9.4, 7.7 Hz), 3.36 (3H, s), 2.19 (1H, d, J = 7.3 Hz), 1.82–1.20, 0.91–0.73 (29H, m), 0.44 (1H, dd, J = 8.7, 6.0 Hz), −0.012 (9H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 76.9, 71.9, 58.9, 31.5, 29.1, 27.4, 13.5, 10.0, 6.6, −0.2. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −0.556. IR (cm^{-1}, neat) 3472–3453, 2955, 2924, 2871, 1463, 1247, 853. HRMS m/e calcd for $C_{16}H_{37}O_2SiSn$ (M − $C_4H_9^+$): 409.1585. Found: 409.1581.

(1S*,3R*)-1-(Tributylstannyl)-1-(trimethylsilyl)hexan-3-ol (50). As in the general procedure, a high pressure hydrogenation bomb with a glass sleeve insert was charged with the substrate (52.4 mg, 0.11 mmol), 20 mol % of the rhodium catalyst (16 mg) and 0.5 mL of dry distilled deaerated dichloromethane. The system was pressurized to 1500 psi and the reaction stirred for 54 h. Following completion of the reaction the catalyst was precipitated by the addition of hexanes, the suspension was filtered through a plug of $MgSO_4$, and the volatiles were removed *in vacuo* to provide **50** (47.7 mg, 91%) of the pure product. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.47 (1H, m), 1.69 (1H, m), 1.52 (18H, m), 0.85 (18H, m), 0.45 (1H, dd, J = 8.6, 6.0 Hz), −0.02 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 73.5, 39.9, 36.2, 29.3, 27.6, 18.9, 14.1, 13.7, 10.2, 7.6, 0.01. ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −3.74. IR (cm^{-1}, neat) 3479, 2959, 2924, 2875, 2854, 1462, 1377, 1244, 1068, 1005, 850. HRMS: Calcd for $C_{21}H_{47}OSiSn$ (M − H^+): 463.2418. Found: 463.2403. Calcd for $C_{20}H_{45}OSiSn$ (M − CH_3^+): 449.2262. Found: 449.2262. Calcd for $C_{17}H_{39}OSiSn$ (M − $C_4H_9^+$): 407.1792. Found: 407.1768.

(2R*,4S*)-4-(Triisopropylsilyl)-4-(trimethylsilyl)butan-2-ol (53). The dried sleeve was charged with **42** (32 mg, 0.11 mmol) and 6 mg (0.0084 mmol, 7 mol %) of the catalyst. Dichloromethane (1 mL) was added and the pressure of hydrogenation was increased to 1500 psi. After 24 h, the catalyst was precipitated by the addition of hexanes and filtered through Na_2SO_4. After removal of volatiles, the residue was redissolved in ether and filtered through silica gel to yield **53** (33 mg, 100%). ^1H NMR (200 MHz, $CDCl_3$) δ: 3.83 (1H, sextet, J = 6.3 Hz), 1.67 (2H, t, J = 6.8 Hz), 1.16 (3H, d, J = 6.1 Hz), 1.31–0.75 (22H, m), 0.21 (1H, dd, J = 7.5, 6.0 Hz), 0.088 (9H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 69.1, 36.9, 22.3, 19.5, 19.2, 12.5, 4.9, 1.5. IR (cm^{-1}, neat) 3447, 2961, 2945, 2867, 1465, 1249, 833. HRMS m/e calcd for $C_{15}H_{35}OSi_2$ (M − CH_3^+): 287.2226. Found: 287.2217.

(2R*,4R*)-4-(Tributylstannyl)-4-(triisopropylsilyl)butan-2-ol (54). As in the general procedure, a glass sleeve insert was charged with the substrate (17.2 mg, 0.03 mmol), 5 mol % of the rhodium catalyst (1.1 mg) and 0.5 mL of dry distilled deaerated dichloromethane. The system was pressurized to 1500 psi and the reaction stirred for 24 h. Following completion of the reaction the catalyst was precipitated by the addition of hexanes, the suspension was filtered through a plug of $MgSO_4$, and the volatiles were removed in vacuo. This gave the 16.4 mg (95%) of the pure product. ^1H NMR (400 MHz, $CDCl_3$) δ 3.66 (1H, m), 1.84 (2H, m), 1.47 (6H, m), 1.29 (7H, m), 1.19 (3H, d, J = 6 Hz), 1.05−1.02 (21H, m), 0.875 (15H, t, J = 7.2 Hz), 0.47 (1H, dd, J = 8.0, 4.4 Hz)). ^{13}C NMR (100 MHz, $CDCl_3$) δ 70.8, 38.7, 29.3, 27.6, 22.3, 19.4, 19.3, 13.6, 12.6, 11.2, 3.2. ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −2.21; IR (cm^{-1}, neat) 3374, 2959, 2924, 2868, 1462, 1377, 1075, 1005, 934, 885, 758; HRMS *m/e* calcd for $C_{21}H_{47}OSiSn$ (M − $C_4H_9^+$): 463.2418. Found: 463.2420.

4,4-Bis(tributylstannyl)butan-2-ol (55). The dried sleeve was charged with **44** (81 mg, 0.13 mmol) and 20 mg (0.028 mmol, ca. 20 mol %) of the catalyst. Dichloromethane (1 mL) was added and the pressure of hydrogenation was increased to 1500 psi. After 44 h, the catalyst was precipitated by the addition of hexanes and filtered through Na_2SO_4. After removal of volatiles, the product was purified by flash chromatography (5% ethyl acetate in hexanes) to yield **55** (45 mg, 55%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.66−3.35 (1H, m), 1.15 (3H, d, J = 6.0 Hz), 2.05−1.65, 1.65−1.02, 0.98−0.47 (58H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 71.5, 40.9, 29.2, 27.5, 13.5, 10.1, 10.0, 23.0, 0.1. ^{119}Sn NMR (74.5 MHz, $CDCl_3$) δ: −8.85, −7.37. IR (cm^{-1}, neat) 3373, 2957, 2924, 2871,1462, 1376, 1070. HRMS *m/e* calcd for $C_{28}H_{61}OSn_2$ (M − H^+): 653.2766. Found: 653.2762.

The monodestannylated product, was also isolated in 12% yield. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.65−3.44 (1H, m), 1.15 (3H, d, J = 6.1 Hz), 1.62−1.10, 0.98−0.61 (32H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 71.2, 36.4, 29.2, 27.4, 22.7, 13.7, 8.8, 4.0. IR (cm^{-1}, neat): 3362, 2958, 2924, 2871,1463, 1376, 1069. HRMS *m/e* calcd for $C_{16}H_{35}OSn$ (M − H^+): 363.1710. Found: 363.1701.

4,4-Bis(trimethylsilyl)butan-2-ol (56). (*Z*)-4-(Trimethylsilyl)-4-(trimethylsilyl)but-3-en-2-ol (12.8 mg, 0.059 mmol) was placed in the flame-dried glass sleeve as indicated in the general procedure, followed by 2.0 mg (4.8 mol %) of the rhodium(I) catalyst and 0.50 mL of deoxygenated dichloromethane. The hydrogenation was carried out at 1500 psi for 16 h and the reaction was worked up to provide **56** (11.2 mg, 87%). ^1H NMR (200 MHz, $CDCl_3$): δ 3.70 (1H, m), 1.57−1.50 (3H, m), 1.15 (3H, d, J = 6.1 Hz), 0.014 (9H, s), 0.010 (9H, s), −0.16 (1H, t, J = 6.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 69.4, 35.9, 23.3, 9.8, 0.13, 0.01. IR (cm^{-1}, neat): 3369, 2967, 1720, 1465, 1294. HRMS *m/e* calcd for $C_9H_{23}OSi_2$ (M − CH_3^+): 203.1287. Found: 203.1281.

Attempted Destannation of (1S*,3S*)-1-Cyclohexyl-3-(tributylstannyl)heptanol (12). The dried sleeve was charged with **12** (16 mg 0.033 mmol) and 2 mg (0.003 mmol, 9 mol %) of the catalyst. Dichloromethane (0.5 mL) was added and the pressure of hydrogen was increased to 1500 psi. After 24 h, the catalyst was removed by filtration through Na_2SO_4. After removal of volatiles, the product was purified by flash chromatography (5% ethyl acetate in hexanes as eluent) to yield 13 mg of **12** (81%) and 1 mg (6%) of the hydrogenolysis product, **13**.

Attempted Destannation of a Mixture of (1S*,3S*)-1-Cyclohexyl-3-(tributylstannyl)heptanol (12) and (1S*,3R*)-1-Cyclohexyl-3-(tributylstannyl)heptanol (23). A 5:1 mixture of **12** and **23** was obtained by oxidation (PCC) of **12** and reduction with $NaBH_4$ (^{119}Sn NMR, −10.58 ppm, major, **12**; −13.46 ppm, minor, **23**). The dried sleeve was charged with the mixture (69 mg, 0.14 mmol) and 5 mg (0.0071 mmol, 5 mol %) of the catalyst. Dichloromethane (0.5 mL) was added and the pressure of hydrogen was increased to 1500 psi. After 24 h, the catalyst was removed by filtration through Na_2SO_4. After removal of volatiles, the product was purified by flash chromatography (5% ethyl acetate in hexanes as eluent) to yield 58 mg of **12** and **23** (85%) and 1.4 mg (5%) of the hydrogenolysis product, **13**. The ^{119}Sn NMR spectrum of the crude product shows two resonances at −10.58 and −13.46 ppm. Their ratio was identical to that of the starting material, i.e. 5:1.

Oxidation of 28 to 34 (R = H). Alkylsilane **28** (29 mg, 0.1 mmol) was dissolved in AcOH (0.5 mL) containing KBr (12 mg, 0.11 mmol). The flask was cooled to 0 °C and AcO_2H (0.5 mL, 32% in AcOH, 2.4 mmol) was added. The mixture was stirred for 20 min before addition of another portion of AcO_2H (1.0 mL, 4.8 mmol). After 2 h stirring at 0 °C, the reaction mixture was diluted with ether and powdered NaS_2O_3 (1 g) was added. The mixture was stirred for 30 min and filtered through Celite. The ether solution was concentrated and washed with aqueous sodium bicarbonate. The aqueous layer was extracted with ether and the combined organics concentrated *in vacuo*. The oil so obtained was purified by chromatography on silica gel (15% ethyl acetate in hexane) to provide 11.4 mg (67%) of the 1,3-diol **34** (R = H), as a pale yellow solid. The spectra of this compound (^1H and ^{13}C NMR) were identical to those of the minor isomer of an authentic sample prepared via the aldol condensation between the boron enolate of acetone and cyclohexanecarboxaldehyde followed by reduction with $Bu_4N^+ BH_4^-$ in acetic acid.[18] ^1H NMR (400 MHz, $CDCl_3$) δSPCLN 4.0 (1H, m), 3.62 (1H, ddd, J = 10.5, 5.3, 2.0 Hz), 2.74 (2H, brs), 1.62−1.80 (5H, m,), 1.57 (1H, dt, J = 14.5, 2.3 Hz), 1.46 (1H, dt, J = 14.3, 10.2 Hz), 1.19 (3H, d, J = 6.2 Hz), 0.95−1.32 (6H, m). ^{13}C NMR δ: (50 MHz, $CDCl_3$) δ: 77.6, 69.4, 44.4, 41.4, 28.7, 27.9, 26.5, 26.2, 26.1.

Oxidation of 28 to 34 (R=Me). In a flame-dried round-bottomed flask, NaH (87 mg, 60% in oil, 2.2 mmol) was washed with *n*-pentane three times before the addition of 1 mL of DMF. After the flask was immersed in an ice bath, **28** (127 mg, 0.44 mmol) in 2 mL of DMF was introduced. The mixture was stirred at 0 °C for 30 min before MeI (1 mL, excess) was added. The ice bath was removed and stirring continued at room temperature for 1.5 h. The resulting mixture was diluted with 1/1 hexane/CH_2Cl_2 and washed with aqueous NH_4Cl, H_2O, and brine. After removal of volatiles and flash chromatography (15% ethyl acetate in hexanes), the methyl ether of **28** was obtained as a colorless oil (108 mg, 81%). ^1H NMR (200 MHz, $CDCl_3$) δ: 7.48−7.52, 7.31−7.35 (5H, 2 m), 3.30 (3H, s), 3.02 (1H, ddd, J = 9.5, 5.1, 2.2 Hz), 1.80−0.87 (15H, m), 0.92 (3H, d, J = 6.0 Hz), 0.24 (3H, s), 0.25 (3H, s). ^{13}C NMR δ: (100 MHz, $CDCl_3$) δ: 138.5, 134.0, 128.7, 127.6, 82.8, 57.7, 41.2, 28.9, 28.5, 26.7, 26.5, 26.4, 32.6, 14.7, 14.0, −4.9,−5.1. IR (cm^{-1}, neat): 3068, 2925, 2954, 2819, 1449, 1248, 1110, 1097. HRMS *m/e* calcd for $C_{18}H_{29}OSi$ (M − CH_3^+): 289.1988. Found: 289.2001.

The methyl ether of **28** (37 mg, 0.12 mmol) was dissolved in AcOH (0.5 mL) containing KBr (19 mg, 0.16 mmol) and NaOAc (29.5 mg, 0.36 mmol). The flask was cooled to 0 °C and AcO_2H (0.15 mL, 32% in AcOH, 0.72 mmol) was added. The mixture was stirred for 20 min before addition of another portion of NaOAc (89 mg, 1.1 mmol) and AcO_2H (0.45 mL, 2.1 mmol). After 3 h at 0 °C, the mixture was diluted with ether and powdered NaS_2O_3 (1 g) was added. The mixture was stirred for 30 min and filtered through Celite. The ether solution was evaporated and the oil so obtained was purified by chromatography on silica gel (15% ethyl acetate/ 85% hexanes) to provide 16 mg (71%) of the differentially protected 1,3-diol **34** (R = Me), as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.92−3.89 (1H, m), 3.35 (3H, s), 3.22 (1H, dt, J = 8.9, 4.2 Hz), 1.68−0.72 (14H, 5m), 1.14 (3H, d, J = 6.2 Hz) ^{13}C NMR δ (100 MHz, $CDCl_3$) δ: 86.9, 68.3, 56.8, 39.8, 38.5 , 29.2, 26.8, 26.7, 26.6, 26.4, 23.7. IR (cm^{-1}, neat): 3382, 2926, 2852, 1450, 1093. HRMS *m/e* calcd for $C_{11}H_{21}O_2$ (M − H^+): 185.1542. Found: 185.1549.

Conversion of 12 to 1,3-Diol. A flask containing iodosobenzene (26.0 mg, 0.12 mmoles) in 0.5 mL of dichloromethane was immersed in an ice bath before the $BF_3{\cdot}Et_2O$ (0.015 mL, 0.12 mmol) was added dropwise. The solids went into solution upon the addition of the $BF_3{\cdot}Et_2O$ to give a clear yellow solution. To the solution was added the acetate ester of **12** (56.8 mg, 0.11 mmol, Ac_2O−Py−DMAP) in 0.5 mL of dry distilled dichloromethane. The resulting solution was stirred at 0 °C until TLC analysis showed the complete consumption

of starting material. Aqueous saturated ammonium chloride (5 mL) was added and the solution stirred vigorously for 0.5 h. Workup was effected by partitioning the reaction mixture between ether and water. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. Filtration followed by concentration *in vacuo* provided a viscous oil which was purified by flash chromatography to yield the desired product and was used immediately in the next reaction.

To a flask containing the stannyl chloride obtained above (50 mg, 0.1 mmol) and K_2CO_3(138 mg, 1.0 mmol) in 0.5 mL of MeOH was added hydrogen peroxide (0.05 mL, 30%). The suspension was stirred at room temperature until TLC showed the absence of starting material. Workup was affected by partitioning of the reaction mixture between ether and water. The aqueous layer was back extracted twice and the combined organics washed with brine and dried over anhydrous magnesium sulfate. Filtration and concentration *in vacuo* yielded an oil which was purified by flash chromatography to yield 3.2 mg (15%) of a white solid. This reaction has not been optimized. Spectra of the product (^{1}H and ^{13}C NMR) were identical to those of the minor isomer of an authentic sample prepared via an aldol condensation between the lithium enolate of 2-hexanone and cyclohexane carboxaldehyde followed by reduction with $NaBH_4$ in acetic acid.[18] The GC retention times of the bis(trimethylsilyl) ethers of the diol from the oxidation reaction and the minor isomer prepared via reduction were identical. ^{1}H NMR (200 MHz, $CDCl_3$) δSPCLN 3.79 (1H, m), 3.58 (1H, m), 3.06 (1H, brs), 2.83 (1H, brs), 0.90–1.80 (22H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 73.1, 69.3, 43.5, 39.2, 28.8, 27.9, 26.3, 26.0, 25.9, 22.5, 13.9.

Acknowledgment. M.L. thanks the A.P. Sloan Foundation, the Natural Science and Engineering Research Council (NSERC) of Canada, BioMega Inc., the Merck Frosst Centre for Therapeutic Research, and the University of Toronto for financial support. We thank Dr. Randolph Belter for preliminary experiments on compound **35** and Patrick Delanghe. C.C. thanks the University of Toronto for an Open Fellowship. Professor R. A. McClelland, University of Toronto, is thanked for very helpful advice with the competition experiments.

Supplementary Material Available: Copies of ^{1}H and ^{13}C NMR spectra of various compounds (60 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.