Organometallics **1996,** *15,* 4469−4472

Direct Access to Unsymmetrical Tin Hydrides through (Hydridodiorganostannio)lithiums

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Received June 4, 1996⊗

Metalation of diorganostannanes $R^1_2SnH_2$ by lithium diisopropylamide afforded the corresponding (hydridodiorganostannio)lithiums, R^1_2SnHLi, which were stable at low temperature. Further reaction with alkyl halides led to functional unsymmetrically substituted alkyldiorganostannanes, $R^1_2R^2SnH$. Tin hydrides with an ω-unsaturated substituent were stable at room temperature. With a 4-pentyl chain, they underwent a specific cyclization process, giving a stannacyclohexane under radical reaction conditions. A tin hydride with a tin−silicon bond could also be prepared.

Introduction

Organotin hydrides are an important class of organotin compounds[1] which have given rise to numerous studies, as they are key intermediates in the preparation of tetraorganotins by hydrostannation and are very convenient reducing agents in organic synthesis.[2] Hydrostannation can be conducted under various conditions involving different mechanisms. That allows, for instance, from the same alkyne the selective preparation of three isomeric adducts: the α-, the (*Z*)-*β*- and the (*E*)-*β*-stannylalkenes,[3] which are also very interesting reagents in organic synthesis for either transmetalation with lithium compounds,[4] or palladium-catalyzed coupling reactions.[5] Numerous applications in organic synthesis have been developed for organotin hydrides as reducing agents. These organotins are particularly interesting, as they can operate under very mild conditions in the presence of numerous functional groups and are efficient not only with bromides and iodides but also with alcohols.[6]

Almost all the applications of organotin hydrides are conducted with tributyltin hydride, because its reactivity scope is wide enough for most studies. However, recent works have shown that more sophisticated hydrides can be useful in organic synthesis either for an improved selectivity or reactivity[7,8] or for practical convenience,[9,10] indicating that research on methods of preparation of organotin hydrides is still of interest. We report here a new access to organotin hydrides involving alkylation of novel (hydridodiorganostannio)lithiums.[11]

Results and Discussion

The main route to triorganotin hydrides involves in the last step the reaction of a tin−heteroatom bond, usually a tin−halogen or a tin−oxygen bond, with reducing agents such as silicon, aluminum, or boron hydrides. This preparation is very convenient in the synthesis of triorganotin hydrides with three identical groups linked to the tin, as the starting materials are easily available from tin tetrachloride in two steps, tetraalkylation and redistribution. When unsymmetrical triorganotin hydrides are required, the preparation is longer, as the monoalkylation of dihalodiorganotins is usually not selective enough to be of preparative use.[12] It involves the alkylation of a diphenyltin dihalide, the cleavage of one phenyl group of the resulting diorganodiphenyltin by hydrochloric acid or bromine, the alkylation of the resulting diorganophenyltin halide, the cleavage of the phenyl group of the unsymmetrical triorganophenyltin and then the reduction step. This long, multistep route could be avoided if the alkylation of (hydridodiorganostannio)lithiums by organic halides were possible. In this method only two steps are required to obtain an unsymmetrical triorganotin hydride from a diorganotin dihalide: reduction of a diorganotin dihalide in diorganotin dihydride and metalation−alkylation. This route saves both time and cost. Moreover, the coupling of a stannyllithium with an organic halide is advantageous in that it avoids the preparation of a Grignard reagent, which may be difficult with some halides,[13] and it is stereospecific, which allows the preparation of optically active organotins with very high enantiomeric excess from optically active halides or tosylates.[14]

Thus, the synthesis of (hydridodiorganostannio)lithiums was attempted. (Triorganostannio)lithiums can be

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⊗ Abstract published in *Advance ACS Abstracts*, September 15, 1996.

[1] Kupchik, E. J. In *Organotin Compounds*; Sawyer, A. K., Ed.; Marcel Dekker: New York, 1971; p 7. Davies, A.; Smith, P. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1979; p 584. Neumann, W. P. *Synthesis* **1987**, 665. Davies, A. In *Comprehensive Organometallic Chemistry*, 2nd ed.; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1995; p 217.

[2] Pereyre, M.; Quintard, J. P.; Rahm A. In *Tin in Organic Synthesis;* Butterworths: London, 1987. Wardell J. L. In *Chemistry of Tin*; Harrison, P. G., Ed.; Blackie: Glasgow, Scotland, 1989; p 315.

[3] Omae, I. *J. Organomet. Chem. Libr.* **1989**, *21*, 171.

[4] Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc*, **1961**, *83*, 3583.

[5] Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. Mitchell, T. N. *Synthesis* **1992**, 803.

[6] Barton, D. H. R.; Motherwell, B. *Pure Appl. Chem.* **1981**, *53*, 15.

[7] Light, J.; Breslow, R. *Tetrahedron Lett.* **1990**, 2957.

[8] Vedejs, E.; Duncan, S. M.; Haight, A. R. *J. Org. Chem.* **1993**, *58*, 3046.

[9] Ferkous, F.; Messadi, D.; De Jeso, B.; Degueil-Castaing, M.; Maillard, B. *J. Organomet. Chem.* **1991**, *420*, 315.

[10] Clive, D. L. J.; Yang, W. *J. Org. Chem.* **1995**, *60*, 2607.

[11] A preliminary account of this work was published in: Connil, M. F.; Jousseaume, B.; Noiret, N.; Pereyre, M. *Organometallics* **1994**, *13*, 24.

[12] Wardell, J. L. In *Chemistry of Tin*; Harrison, P. G., Ed.; Blackie: New York, 1989; p 146. See for instance: Marr, I. L.; Rosales, D.; Wardell, J. L. *J. Organomet. Chem.* **1988**, *349*, 65.

[13] Wakefield, B. J. In *Organomagnesium Methods in Organic Synthesis*; Academic Press: London, 1995.

S0276-7333(96)00444-X CCC: $12.00

prepared by reaction of lithium with organotin chlorides[15] or organoditins,[16] by reaction of lithium reagents with organoditins,[17] or by metalation of organotin hydrides by lithium diisopropylamide.[18] In our case, the first two methods require the preparation of unstable or unknown organotins, while the third one involves easily available diorganotin dihydrides.[19] Thus, dibutyltin dihydride was treated with a THF−hexane solution of lithium diisopropylamide, as in the procedure developped by Still for the preparation of (triorganostannio)lithiums[18] (see Scheme 1). After a few minutes, methyl iodide was added. However, analysis of the reaction mixture only revealed the presence of tributyltin hydrides and cyclopolytins.[20] The same reaction was then conducted at lower temperature, and its analysis was more gratifying, as it led to the isolation of methyldibutyltin hydride in 45% yield. It was thus possible to prepare an unsymmetrical triorganotin hydride in this way.

Scheme 1

$$Bu_2SnH_2 + iPr_2NLi \xrightarrow{-iPr_2NH} Bu_2SnHLi \xrightarrow{MeI} MeBu_2Sn$$

The existence of a (hydrodiorganostannio)lithium intermediate was checked by its reaction with deuterium oxide. Addition of deuterium oxide to a solution of dibutyltin dihydride which had been treated with lithium diisopropylamide gave deuteriodibutylstannane, which appeared as a statistical mixture of dibutyltin dihydride, deuteriodibutyltin hydride and dibutyltin dideuteride (70% yield) (Scheme 2). Deuterium incorporation was higher than 95%. This mixture was characterized by ^{119}Sn NMR. Three resonances at −204.0, −205.2, and −206.4 ppm, corresponding to a statistical distribution of dibutyltin dihydride, deuteriodibutyltin hydride, and dibutyltin dideuteride, respectively, were recorded.

Scheme 2

$$Bu_2SnH_2 + iPr_2NLi \xrightarrow{-iPr_2NH} Bu_2SnHLi \xrightarrow{D_2O} Bu_2SnHD$$

Both experiments established the existence of a new (organostannio)lithium, (hydridodibutylstannio)lithium. In germanium[21] and silicon[22] chemistry, (hydridogermanio) and (hydridosilicio)lithiums have been reported recently, and in tin chemistry an example of a very hindered reagent of the same type, [(2,4,6-tris(bis(trimethylsilyl)methyl)phenyl)(2,4,6-triisopropylphenyl)hydridostannio]lithium,[23] has been independently[11] obtained by the metalation of the corresponding dihydride by *tert*-butyllithium. The potential application of this new (hydridodibutylstannio)lithium in the synthesis of unsymmetrical triorganotin hydrides was tested with other halides and extended to other diorganotin dihydrides. The coupling with a bromide, 1-bromopropane, was attempted first. It gave the corresponding tin hydride, propyldibutyltin hydride, in good yield (60% yield). 1-Chloropropane gave equally good results (57% yield).

The reaction was not limited to dibutyltin dihydrides. It was general and could be extended to other hydrides, such as dicyclohexyltin and diphenyltin dihydrides. These (hydridostannio)lithiums coupled with 1-bromopropane to give dicyclohexylpropyltin and diphenylpropyltin hydrides, respectively (Scheme 3).

Scheme 3

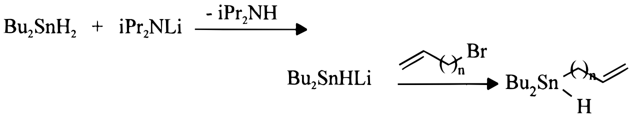
$$R_2SnH_2 + iPr_2NLi \xrightarrow{-iPr_2NH} R_2SnHLi \xrightarrow{PrBr} PrR_2SnH$$

R (% yield): c-C_6H_{11} (63), Ph (50)

The usefulness of this preparation of tin hydrides was exemplified in the synthesis of tin hydride supported reagents by the coupling of (hydridodibutylstannio)lithium with halogenated polystyrene, which allowed a direct grafting of tin hydride units.[24]

The coupling worked equally well with ω-alkenyl bromides and gave previously unreported ω-alkenyldibutyltins in good yield with two, three, or four methylene units between the tin and the double bond (Scheme 4). Heating the unsaturated hydrides led to mixtures of cyclized and oligomerized compounds.

Scheme 4



n (% yield) = 2 (72), 3 (67), 4 (71)

This cyclization process was studied in detail, as it could be a new entry to stannacycloalkanes. Organostannyl radicals are well-known to add to olefinic double bonds. Free-radical addition to carbon−carbon double bonds can also occur intramolecularly, resulting in cyclic products. Reactions with ω-alkenyldibutyltins were run in sealed, degassed tubes in benzene using azobisisobutyronitrile (AIBN) as initiator at 110 °C for 12 h (Scheme 5). With 4-pentenyldibutyltin, the only

Scheme 5

cyclization product was 1,1-dibutyl-1-stannacyclohex-

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[14] Jensen, F. R.; Davies, D. D. *J. Am. Chem. Soc,* **1971**, *93*, 4047. San Filippo, J.; Silbermann, J. *J. Am. Chem. Soc.* **1981**, *103*, 5588. Lee, K. W.; San Filippo, J. *Organometallics* **1982**, *1*, 1496. San Filippo, J.; Silbermann, J. *J. Am. Chem. Soc.* **1982**, *104*, 2831. Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833. Lucas, C.; Santini, C.; Printz, M.; Basset, J. M.; Connil, M. F.; Jousseaume, B. *J. Organomet. Chem.*, in press.

[15] Gilman, H.; Mars, O. L.; Sim, S. Y. *J. Org. Chem.* **1962**, *27*, 4232.

[16] Tamborski, C.; Ford, F. E.; Soloski, E. J. *J. Org. Chem.* **1963**, *28*, 237.

[17] Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4836.

[18] Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481.

[19] Van der Kerk, G. J. M.; Noltes, J. G.; Luijten, J. G. A. *J. Appl. Chem.* **1957**, *7*, 366.

[20] Jousseaume, B.; Noiret, M.; Pereyre, A.; Saux, A. *Organometallics* **1994**, *13*, 1034.

[21] Castel, A.; Rivière, P.; Satgé, J.; Ko, Y. H. *Organometallics* **1992**, *9*, 205.

[22] Roddick, D. M.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 324.

[23] Matsuhashi, Y.; Tokitoh, N.; Okazaki, R.; Goto, M.; Nagase, S. *Organometallics* **1993**, *12*, 1351.

[24] Dumartin, G.; Ruel, G.; Kharboutli, J.; Delmond, B.; Connil, M. F.; Jousseaume, B.; Pereyre, M. *Synlett* **1994**, 952.

ane,[25] obtained in quantitative yield. No 1,1-dibutyl-2-methyl-1-stannacyclopentane was detected. In contrast, 3-butenyldibutyltin hydride and 5-hexenyldibutyltin hydride gave the corresponding cyclized compounds in low yields only, and large quantities of uncyclized tin hydrides were recovered.

The present results of the ring closure reaction of the 4-pentenyldibutylstannyl radical are clearly different from those of the corresponding 5-hexenyl- and 4-pentenylsilyl and 4-pentenylgermyl radicals. The 5-hexenyl radical[26] cyclizes to give a mixture of five- and six-membered rings. This process can be driven to give the five-membered ring by varying the reaction conditions. The silylated[27] and germylated[28] analogs show a different behavior: they lead in only low yield to mixtures of five-and six-membered rings where the six-membered ring predominates. The larger atomic radius of tin and the longer tin–carbon bonds could favor the formation of the six-membered ring by changing the stability of both transition states and cyclic radicals. The reversibility of organotin radical attack on olefins[29] could also favor the isomerization of the five-membered radical to the six-membered radical, leading to the stereospecific formation of the six-membered ring. In contrast, the addition of silyl and germyl radicals is an irreversible process. This method provides an interesting alternative to the known preparation of stannacyclohexanes,[30] involving the decomposition of α,ω-distannylalkanes in the presence of zinc chloride[25] or the use of dimagnesium halide derivatives[31] which give these cyclic derivatives together with oligomers and polymers.

Organotin hydrides with an organic group substituted by polar substituents recently had interesting applications in organic synthesis. Tributyltin hydride is widely used in preparative free-radical chemistry. However, product isolation is sometimes difficult because compounds containing tin formed in these reactions are not always easily separated from the organic products. To overcome this difficulty, several organotin hydrides substituted by heteroatoms have been prepared. Three organic groups can be substituted by ethylene glycol ether units, as in tris[3-(2-methoxyethoxy)propyl]tin hydride.[7] This results in a high water solubility of the tin hydride and allows an easy separation from organic compounds simply by water extraction. When one organic group is substituted by ethylene glycol ether units, as in dibutyl(4,7,10-trioxaundecyl)tin hydride,[9] or by a pyridyl group, as in diphenyl(2-pyridylethyl)tin hydride,[10] the corresponding hydride can be separated from organic compounds by chromatography on silica gel. Substitution by heteroatoms is useful for reasons other than solving separation problems. The introduction of a heteroatom can modify the reactivity of the corresponding tin hydride. A dimethylamino group in the γ-position from the metal increases the reactivity of [2-(dimethylamino)phenyl]dimethyltin hydride,[8] which can serve as a selective nucleophilic hydride source or as a radical reducing agent at room temperature. All these new hydrides are prepared according to the classical way: introduction of the substituted organic group via its Grignard or lithium reagent and transformation of the resulting organotin halide to the tin hydride. The use of (hydridodibutylstannio)lithium provides substituted triorganotin hydrides directly from diorganotin dihydrides and methoxylated halides, 1-bromo-4-methoxybutane and 1-bromo-5,8-dioxanonane, in good yields (Scheme 6).

Scheme 6

$$\mathrm{Bu_2SnHLi} \xrightarrow{\mathrm{Br(CH_2)}_m\mathrm{(OCH_2CH_2)}_n\mathrm{OMe}} [\mathrm{MeO(CH_2CH_2O)}_n\mathrm{(CH_2)}_m]\mathrm{Bu_2SnH}$$

$m = 4$, $n = 0$, yield 45%; $m = 4$, $n = 1$, yield 67%

While silicon–tin-bonded derivatives were described as early as 1933,[32] a similar bimetallic hydride with a silicon–hydrogen bond was prepared only recently by the coupling of (tributylstannio)lithium with chlorodimethylsilane.[33] To our knowledge, no similar bimetallic hydride with a tin–hydrogen bond has been prepared. Bimetallic hydrides are of interest in radical reactions, as it was shown that, with silicon hydrides, substitution of an organic group on silicon by a trimethylsilyl group weakens the silicon–hydride bond and thus enhances the hydrogen transfer process in radical reactions. Tris(trimethylsilyl)silane is a valuable reagent in free-radical processes.[34] The coupling of (hydridodicyclohexylstannio)lithium with chlorotriisopropylsilane gave (triisopropylsilyl)dicyclohexyltin hydride (Scheme 7). This reaction has also been used by others to prepare (trimethylsilyl)dibutyltin hydride,[35] which again demonstrates the preparative utility of (hydridodiorganostannio)lithiums.

Scheme 7

$$\mathrm{Cy_2SnHLi} \xrightarrow{\mathrm{iPr_3SiCl}} \underset{42\%}{\mathrm{Cy_2(iPr_3Si)SnH}}$$

In conclusion, it has been shown that (hydridodiorganostannio)lithiums can be easily prepared from various diorganotin dihydrides and lithium diisopropylamide. They are stable at low temperature and decompose on heating to the corresponding triorganotin hydrides and poly(diorganotins). The coupling with functional organic and organosilicon halides gives new functional unsymmetrical triorganotin hydrides in a particularly direct way.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Pentane, THF, and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Diisopropylamine was distilled from calcium hydride. Dibutyl- and diphenyltin hydrides were prepared by reduction of the corresponding dichlorides by lithium aluminum hydride.[36] 1-Bromo-3-butene, 1-bromo-4-pentene, and 1-bromo-5-hexene were obtained from

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(25) Bulten, E. J.; Budding, H. A. *J. Organomet. Chem.* **1976**, *110*, 167.

(26) Lamb, R. C.; Ayers, P. W.; Toney, M. K. *J. Am. Chem. Soc.* **1963**, *85*, 3483. Julia, M. *Acc. Chem. Res.* **1971**, *4*, 386.

(27) Sakurai, H. In *Free Radicals*; Kochi, J., Ed.; Wiley: New York, 1973; p 793.

(28) Mochida, K.; Asami, K. *J. Organomet. Chem.* **1982**, *232*, 13.

(29) Kuivila, H. G.; Sommer, R. *J. Am. Chem. Soc.* **1967**, *89*, 5616.

(30) Pant, B. C. *J. Organomet. Chem.* **1974**, 66, 321.

(31) Davies, A.; Tse, M. W.; Kennedy, J. D.; McFarlane, W.; Ladd, M. F. C.; Povey, D. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 369.

(32) Kraus, C. A.; Eatough, H. *J. Am. Chem. Soc.* **1933**, *55*, 5003.

(33) Ikenaga, K.; Hiramatsu, K.; Nasaka, N.; Matsumodo, S. *J. Org. Chem.* **1993**, *58*, 5045.

(34) Ballestri, M.; Chatgilialoglu, C.; Clark, K. B.; Griller, D.; Giese, B.; Kopping, B. *J. Org. Chem.* **1991**, 56, 678. Chatgilialoglu, C. *Acc. Chem. Res.* **1992**, 25, 188.

(35) Mitchell, T. Private communication.

(36) Creemers, H. M. J. C. Dissertation, University of Utrecht, 1967.

the corresponding ω-dibromoalkane.[37] 1-Bromo-4-methoxybutane and 1-bromo-5,8-dioxanonane were prepared according to known procedures.[38] ^{1}H NMR spectra and ^{13}C NMR spectra were taken on a Bruker AC-250 spectrometer (solvent C_6D_6, internal reference Me_4Si); ^{119}Sn NMR spectra were recorded on a Bruker AC-200 spectrometer (solvent C_6D_6, internal reference Me_4Sn). ^{119}Sn−H and ^{119}Sn−C coupling constants (in Hz) are given in brackets.

Dicyclohexyltin Dihydride. In a three-necked flask was placed chlorotrimethylsilane (100 g, 0.92 mol), and tricyclohexyltin hydroxide (40 g, 0.11 mol) was slowly added. The mixture was heated at reflux for 12 h. Chlorotrimethylsilane and hexamethyldisiloxane were distilled off, and tricyclohexyltin chloride was recrystallized from petroleum ether (mp 129 °C, 29.7 g, 67%). A solution of bromine (8.7 g, 54 mmol) in 25 mL of chloroform was slowly added to tricyclohexyltin chloride (22 g, 54 mmol) in 75 mL of chloroform. The mixture was heated at reflux for 4 h. After evaporation of the solvent, bromodicyclohexyltin chloride was recrystallized from ethanol (mp 68 °C, 10.8 g, 50%). To a slurry of lithium aluminum hydride (4.4 g, 110 mmol) in 125 mL of dry diethyl ether under nitrogen at 0 °C was added a solution of bromodicyclohexyltin chloride (28 g, 70 mmol). The mixture was refluxed for 2 h. After addition of 100 mL of petroleum ether, the mixture was hydrolyzed slowly with a saturated solution of ammonium chloride. The resulting solution was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. Dicyclohexyltin dihydride was purified by distillation (12.6 g, 63%, bp 110 °C (10^{-4} mm)). ^{1}H NMR δ 1.20−1.82 (m, 22H), 4.97 (s, 2H, [1591]). ^{13}C NMR: δ 25.6 [390], 27.4, 29.1 [56], 33.6 [17]. ^{119}Sn NMR: δ −180.9.

Coupling of (Hydridodiorganostannio)lithiums with Organic Halides. In a Schlenk tube under nitrogen, a solution of *n*-butyllithium (8.4 mL, 21 mmol, 2.5 M in hexanes) was added to a solution of diisopropylamine (2.12 g, 21 mmol) in 50 mL of anhydrous THF, at 0 °C. After the mixture was stirred for 15 min, the temperature was lowered to −70 °C and the diorganotin dihydride (20 mmol) was added dropwise. The mixture was stirred for 30 min at −50 °C and the halide (20 mmol) added. The mixture was warmed to 0 °C, diluted with 50 mL of petroleum ether, and hydrolyzed by dropwise addition of water. The aqueous layer was separated and extracted twice with 20 mL of petroleum ether. The organic layer was washed with water and dried over anhydrous $MgSO_4$. The solvents were evaporated, and the corresponding triorganotin hydrides were purified by distillation in a Kugelrohr apparatus. Methyldibutyltin hydride:[39] yield 40%; bp 45 °C (0.1 mm); ^{1}H NMR δ 0.05 (d, 3H, [45]), 0.90 (m, 10H), 1.41 (m, 4H), 4.88 (m, 1H); ^{13}C NMR δ −13.7 [317], 8.3 [362], 13.7, 27.1 [132], 30.0 [53]. Anal. Calcd for $C_9H_{22}Sn$: C, 43.37; H, 8.83. Found: C, 42.12; H, 8.47. *n*-Propyldibutyltin hydride: yield 60%; bp 60 °C (0.1 mm);^{1}H NMR δ 0.9 (m, 15H), 1.30 (m, 4H), 1.55 (m, 6H), 4.85 (m, 1H); ^{13}C NMR δ 8.5 [326], 11.2 [328], 13.7, 18.4 [52], 21.3 [22], 27.9 [52], 30.3 [22]; ^{119}Sn NMR δ −89.0. Anal. Calcd for $C_{11}H_{26}Sn$: C, 47.69; H, 9.46. Found: C, 47.12; H, 9.14. *n*-Propyldiphenyltin hydride: yield 50%; bp 110 °C (0.001 mm); ^{1}H NMR δ 0.90 (t, 3H), 1.21 (t, 2H, [54]), 1.62 (m, 2H, [55]), 6.34 (m, 1H), 7.29 (m, 10H); ^{13}C NMR δ 13.1 [380], 18.3 [60], 20.8 [22], 128.8, 129.1 [11], 129.2, 137.5 [36]; ^{119}Sn NMR δ −137. Anal. Calcd for $C_{15}H_{18}Sn$: C, 56.83; H, 5.72. Found: C, 56.38;H, 5.27. *n*-Propyldicyclohexyltin hydride: yield 63%; bp 120 °C (0.001 mm); ^{1}H NMR δ 0.93 (m, 2H), 1.02 (t, 3H), 1.25−1.90 (m, 24H), 5.15 (s, 1H); ^{13}C NMR δ 10.0 [309], 19.2 [51], 21.8 [22], 25.8 [362], 27.4, 29.2 [54], 33.2 [16], 33.3 [16]; ^{119}Sn NMR δ −87.9. Anal. Calcd for $C_{15}H_{30}Sn$: C, 54.75; H, 9.19. Found: C, 54.98; H, 8.95. 3-Butenyldibutyltin hydride: yield 72%; bp 60 °C (0.001 mm); ^{1}H NMR δ 0.74 (m, 12H), 1.15 (m, 4H), 1.41 (m, 4H), 1.87 (q, 2H, [48]), 4.52 (m, 1H), 4.79 (dd, 1H), 4.82 (dd, 1H), 5.55−5.62 (m, 1H); ^{13}C NMR δ 7.8 [335], 8.7 [343], 14.0, 27.6 [54], 30.4 [21], 32.1 [19], 113.4, 141.5; ^{119}Sn NMR δ −86.2. Anal. Calcd for $C_{12}H_{26}Sn$: C, 49.87; H, 9.07. Found: C, 48.42; H, 8.84. 4-Pentenyldibutyltin hydride: yield 67%; bp 60 °C (0.001 mm); ^{1}H NMR δ 0.88 (m, 12H), 1.29 (m, 4H), 1.48 (m, 6H), 2.25 (q, 2H, [49]), 4.67 (m, 1H), 4.96 (dd, 1H), 5.02 (dd, 1H), 5.87 (m, 1H); ^{13}C NMR δ 8.2 [337], 8.5 [341], 14.0, 27.7 [53], 30.4 [22], 31.1 [24], 38.7 [55], 114.8, 138.5; ^{119}Sn NMR δ −87.2. Anal. Calcd for $C_{13}H_{28}Sn$: C, 51.52; H, 9.31.Found: C, 50.87; H, 8.95. 5-Hexenyldibutyltin hydride: yield 71%; bp 85 °C (0.001 mm); ^{1}H NMR δ 0.89 (m, 12H), 1.33 (m, 6H), 1.52 (m, 6H), 1.99 (q, 2H), 4.67 (m, 1H), 4.96 (dd, 1H), 5.02 (dd, 1H), 5.85 (m, 1H); ^{13}C NMR δ 8.5 [338], 14.1, 27.7 [54], 30.6 [21], 33.9 [53], 34.0, 114.5, 138.9; ^{119}Sn NMR δ −87.9. Anal. Calcd for $C_{14}H_{30}Sn$: C, 53.03; H, 9.54. Found: C, 53.15; H, 9.09. (4-Methoxybutyl)dibutyltin hydride: yield 45%; bp 90 °C (0.001 mm); ^{1}H NMR δ 0.90 (m, 12H), 1.28−1.69 (m, 12H), 3.13 (s, 3H), 3.24 (t, 2H), 5.04 (m, 1H); ^{119}Sn NMR δ −66.0. Anal. Calcd for $C_{13}H_{30}OSn$: C, 48.63; H, 9.42. Found: C, 49.47; H, 9.07. (5,8-Dioxanonyl)dibutyltin hydride: yield 43%; bp 125 °C (0.001 mm); ^{1}H NMR δ 0.88 (m, 12H), 1.32 (m, 4H), 1.60 (m, 8H), 3.14 (s, 3H), 3.33 (m, 6H), 4.96 (m, 1H); ^{13}C NMR δ 8.3 [337], 13.8, 24.7 [25], 27.4 [55], 30.2 [29], 34.6 [44], 58.7, 70.5, 70.9, 72.4. Anal. Calcd for $C_{15}H_{34}O_2Sn$: C, 49.34; H, 9.39. Found: C, 48.75; H, 9.02.

Coupling of (Hydridodibutylstannio)lithium with Polystyrene-Supported Chloride. Dibutyltin dihydride (7.75 g, 33 mmol) was slowly added to a THF (20 mL)-hexane (12 mL) solution of lithium diisopropylamide (30 mmol) at −70 °C. After 30 min at −50 °C this solution was transferred into a Schlenk tube containing 5 g (11.15 mmol of Cl) of poly[(4-chlorobutyl)styrene] in 20 mL of THF, at −70 °C. The mixture was warmed to −10 °C over 12 h. The polymer was washed with THF (50 mL), THF/H_2O (4/1; 20 mL), THF (5 × 40 mL), and ethanol (3 × 40 mL) and was dried under vacuum. IR: ν_{Sn-H} 1800 cm^{-1}. The poly[(4-(dibutylstannyl)butyl)styrene] contained 1.4 mmol of Sn/g (% Sn 17.01).

Alkenyltin Hydride Cyclizations. Alkenyldiorganotin hydride (2 mmol), AIBN (5 mg), and heptane (35 mL) were placed in a glass tube. The tube was sealed after degassing and placed in an oven (110 °C, 12 h). After evaporation of heptane the residue was analyzed by ^{119}Sn NMR spectroscopy: dibutylstannacyclopentane,[25] δ 54.5; dibutylstannacyclohexane,[25] δ −50.1; dibutylstannacycloheptane,[25] δ 0.2. Dibutylstannacyclohexane: ^{1}H NMR δ 1.8−1.2 (m, 14H), 0.8−1.05 (m, 14H); ^{13}C NMR δ 8.9 [138], 9.0 [153], 13.8, 27.8 [56], 28.7 [27], 29.9 [20], 32.5 [43].

(Triisopropylsilyl)dicyclohexylstannane. In a Schlenk tube under nitrogen, a solution of *n*-butyllithium (8.4 mL, 210 mmol, 2.5 M in hexanes) was added to a solution of diisopropylamine (2.12 g, 21 mmol) in 50 mL of anhydrous THF at 0 °C. After the mixture was stirred for 15 min, the temperature was lowered to −70 °C and dicyclohexyltin dihydride (5.74 g, 20 mmol) was added dropwise. The mixture was stirred for 30 min at −50 °C and the halide (3.84 g, 20 mmol) added. This mixture was warmed to 0 °C. Petroleum ether (50 mL) was added, and then the mixture was hydrolyzed by dropwise addition of water. The organic layer was separated, the solvents were evaporated, and chromatography of the residue under nitrogen (alumina, petroleum ether) gave the desired product. Yield: 42%. HRMS: *m/z* 443.2153 (M − H), calcd 443.2156. ^{1}H NMR: δ 1.11 (m, 21H), 1.30−1.68 (m, 22H), 4.50 (s, 1H). ^{13}C NMR; δ 14.2, 20.7, 26.8 [277], 27.6, 30.1 [53], 30.2 [53], 34.7 [14], 35.4 [14]. ^{119}Sn NMR: δ −196.6.

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(37) Kraus, G. A.; Landgrebe, K. *Synthesis* **1984**, 885.

(38) Kirrmann, A.; Hamaide, N. *Bull. Soc. Chim. Fr.* **1957**, 789.

(39) Martin-Lauda, I.; De Pablos, F.; Marr, I. L. *Anal. Proc.* **1989**, *26*, 16.