Synthesis and Free Radical Addition Reactions of Tris[(phenyldimethylsilyl)methyl]tin Hydride

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Received November 12, 2002

The synthesis of the new bulky tris[(phenyldimethylsilyl)methyl]tin hydride (**9**), tetrakis[(phenyldimethylsilyl)methyl]tin (**5**), and hexakis[(phenyldimethylsilyl)methyl]ditin (**10**) as well as some physical properties are described. The addition of hydride **9** to seven mono- and disubstituted alkynes under radical conditions indicates that these reactions take place with complete stereoselectivity. Full ^{1}H, ^{13}C, ^{119}Sn, and ^{29}Si NMR characteristics are included.

Introduction

Organotin hydrides have found many applications in organic synthesis not only as reducing reagents but also as intermediates in the generation of carbon−carbon bonds, and for the preparation of compounds such as vinylstannanes, which are invaluable starting materials for cross-coupling reactions.[1] In previous studies we have shown that the size of the organic ligands attached to the tin atom affects not only the reactivity but also the stereoselectivity of the reactions of these compounds.[2] Thus we reported the synthesis and reactions of organotin compounds containing neophyl and (−)-menthyl ligands.

In trineophyltin derivatives, the binding of the bulky neophyl ligands to tin causes a serious distortion from tetrahedral geometry. Thus, in trineophyltin chloride the angles C−Sn−C are 117.2° (mean), whereas the C−Sn−Cl angle is 99.7°.[3] Replacement of the central carbon atom of the neophyl ligands by silicon leads to the tris(phenyldimethylsilylmethyl)tin chloride (**3**) and to a decrease in steric strain because of a smaller distortion from the tetrahedral geometry: C−Sn−C angles 113.3° (mean) and C−Sn−Cl 105.3°.[3] Taking into account these facts, and following our investigations on the relationship between the steric volume of the substituents attached to the tin atom and the reactivity as well as the stereoselectivity of organotin compounds, we considered it to be of interest to carry out the synthesis of tris[(phenyldimethylsilyl)methyl]tin hydride (**9**) and to study some reactions of this new bulky tin hydride.

Results and Discussion

Our initial synthetic goal was to prepare tris[(phenyldimethylsilyl)methyl]tin chloride (**3**), which, upon reduction, should lead to the desired tin hydride. To obtain **3**, tin tetrachloride was alkylated with (phenyldimethylsilyl)methylmagnesium bromide (**2**) according to Tacke et al.[4] (Scheme 1). We repeated the reaction using the ratio Grignard reagent/$SnCl_4$ = 3:1 six times, always obtaining a mixture of chloride **3** and bis[(phenyldimethylsilyl)methyl]tin dichloride (**4**) in an average ratio **3**/**4** = 13.3:1 with an overall yield of 91%, as shown by ^{119}Sn NMR spectroscopy. These mixtures were very soluble in methylene chloride, diethyl ether, hexane, cyclohexane, and petroleum ether, even at low temperatures (0 to −23 °C). Unlike Tacke, we were unable to recrystallize **3** pure from these mixtures.

Taking into account these results, we decided to carry out a study of the reaction under different conditions. This study demonstrates (Table 1) that the tetraorganotin compound **5** is the only derivative with phenyldimethylsilylmethyl ligands that could be obtained pure by alkylation of tin tetrachloride using an appropriate Grignard reagent/$SnCl_4$ ratio. It should be noted that it is not possible to obtain the triorganotin halide from **5** by halogenation because this reaction leads to the cleavage of the Si−Ph bond. Table 1 shows that, according to the ratio **2**/$SnCl_4$, in most cases we obtained varying mixtures of chlorides **3** and **4**, and the tetraorganotin (**5**). These reactions were carried out by using titrated solutions of **2** in diethyl ether. The results obtained are summarized in Table 1. In all but one

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(1) (a) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987. (b) Davies, A. *Organotin Chemistry*; VCH: Weinheim, 1997. (c) Mitchell, T. N. Organotin Reagents in Cross-Coupling. Chapter 4 in *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany. (d) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon−Carbon Bonds*; Pergamon Press: Oxford, 1986. (e) Marshall, J. A. Organotin Chemistry. In *Organometallics in Synthesis: A Manual*; Schlosser, M., Ed.; John Wiley & Sons Ltd: New York, 2002.

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10.1021/om020936b CCC: $25.00

Scheme 1

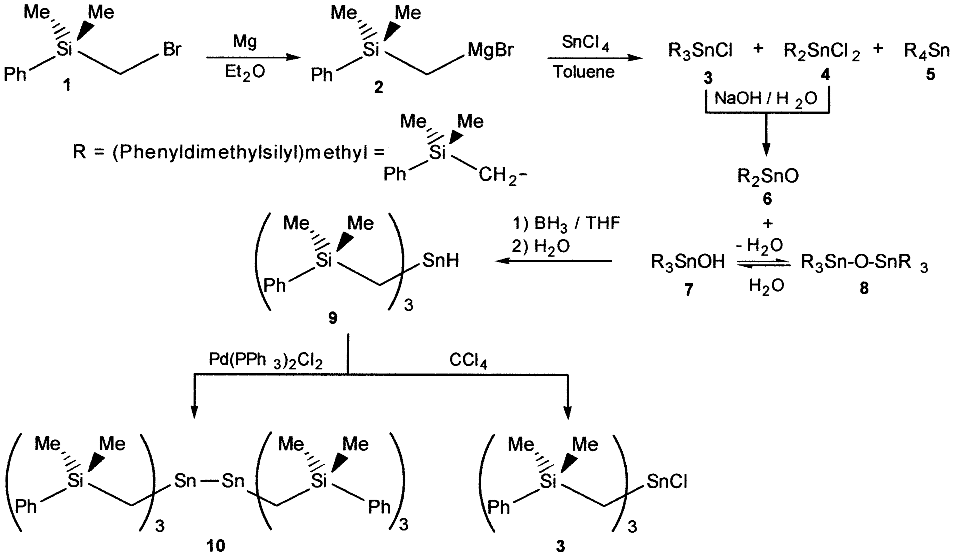

Table 1. Tin Tetrachloride Alkylation under Different Conditions

entry	**2**/$SnCl_4$ ratio	reaction conditions[a]	yield (%)	product relationships (%)[b]		
				R_3SnCl (**3**)	R_2SnCl_2 (**4**)	R_4Sn (**5**)
1	2.6	(1) rt; (2) rt 15 h; (3) refx. 3 h	81	12.5	76.6	10.9
2	3.0	(1) rt; (2) rt 15 h; (3) refx. 3 h	82	23.5	5.9	70.6
3	3.0	(1) 0 °C; (2) rt 1.5 h; (3) refx. 3 h	91	93.0	7.0	
4[c]	3.0	(1) 0 °C; (2) rt 1.5 h; (3) refx. 3 h	89	35.7	9.3	55.0
5[d]	3.0	(1) 0 °C; (2) rt 1.5 h; (3) refx. 3 h	91	30.8	11.2	58.0
6	3.0	(1) 0 °C; (2) rt 1.5 h; (3) refx. 8 h	93	39.0	13.2	47.8
7	3.1	(1) rt; (2) rt 15 h; (3) refx. 3 h	82	37.5	6.3	56.2
8	3.1	(1) 0 °C; (2) rt 1.5 h; (3) refx. 3 h	92	82.5	15.6	1.9
9	3.2	(1) 0 °C; (2) rt 1.5 h; (3) refx. 3 h	92	81.7	12.4	5.9
10	4.1	(1) rt; (2) rt 15 h; (3) refx. 3 h	100			100
11	5.1	(1) 0 °C; (2) rt 12 h; (3) refx. 3 h	92			100

[a] All the reactions were carried out by adding the Grignard reagent (GR) in diethyl ether onto a solution of $SnCl_4$ in toluene, except when otherwise stated; rt = room temperature; refx. = reflux. [b] From ^{119}Sn NMR spectra. [c] The solution of $SnCl_4$ in toluene was added to the GR in ether. [d] $SnCl_4$ was added in benzene.

experiment (entry 4) the Grignard reagent was added dropwise to the solution of tin tetrachloride in toluene.

In view of these results, we decided that in order to obtain the organotin hydride it might be convenient first to convert the mixture of chlorides **3** and **4**, obtained under the conditions of entry 3 (Table 1), into the mixture of the corresponding stannoxanes by treatment with sodium hydroxide (Scheme 1) and then to attempt the separation of the equilibrium mixture of hydroxide **7** and oxide **8** from oxide **6**. Much to our surprise we found that the ^{119}Sn NMR spectrum of the crude product showed only the peaks corresponding to a mixture of compounds **7** and **8**. This might be connected either with the solubility of oxide **6** in water or to its insolubility in both water and ether.

This result simplified the route to tris[(phenyldimethylsilyl)methyl]tin hydride (**9**) because by reduction of the mixture of compounds **7** and **8** with borane in THF,[5] as shown in Scheme 1, the desired tris[(phenyldimethylsilyl)methyl]tin hydride (**9**) was obtained. In summary, the direct conversion of the mixture of chlorides **3** and **4**, obtained from the alkylation of tin tetrachloride with the Grignard reagent **2**, into the mixture of **7** and **8** by treatment with sodium hydroxide, followed by the reduction of the mixture with borane in THF led to tris[(phenyldimethylsilyl)methyl]tin hydride (**9**) in 89% yield (based on tin tetrachloride used).

It can also be seen from Scheme 1 that while the reaction of hydride **9** with CCl_4 and $CDCl_3$ leads to the corresponding chloride **3**, leaving this hydride in benzene at 40 °C in argon atmosphere and in the presence of catalytic amounts of bis(triphenylphosphine)palladium dichloride gives hexakis[(phenyldimethylsilyl)-methyl]ditin (**10**) in 74% yield.

The main spectroscopic characteristics of the new compounds are summarized in Tables 2 and 3. In these tables we have also included the characteristics of bis-[(phenyldimethylsilyl)methyl]tin dichloride (**4**) because, although this compound has already been reported,[6] Chinese literature is often not readily available.

To test the possibility of carrying out stereoselective hydrostannations using hydride **9** under radical conditions, we carried out the addition of this hydride to some terminal and internal alkynes. Taking into account previous work,[2f] we considered it possible that under radical conditions the main products of these reactions should be those corresponding to an *anti* addition of the tin hydride (**A-1** and **A-2**), as shown in Table 4.

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(5) Chopa, A. B.; Koll, L. C.; Podestá, J. C.; Thorpe, F. G. *Synthesis* **1983**, 722.

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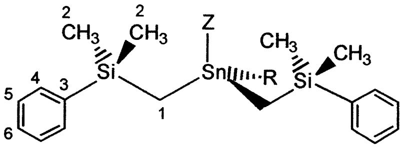
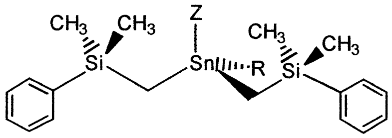
Table 2. ^{13}C NMR Data of Compounds 4, 5, 9, and 10[a]



compd no.	R	Z	C(1) [^1J(Sn,C)] [^1J(Si,C)]	C(2) [^3J(Sn,C)] [^1J(Si,C)]	C(3) [^3J(Sn,C)]	C(4)	C(5)	C(6)
4	Cl	Cl	11.79 (278.0) (nd)	−0.94 (54.4) (23.3)	138.27 (32.7)	133.25	129.51	128.03
5	$PhMe_2SiCH_2$	$PhMe_2SiCH_2$	−2.86 (239.1) (33.9)	0.29 (52.5) (12.9)	144.21 (21.1)	133.20	128.62	127.60
9	$PhMe_2SiCH_2$	H	−5.41 (252.7) (nd)	−0.56 (52.5) (15.5)	140.56 (18.5)	133.40	128.79	127.10
10	$PhMe_2SiCH_2$	$(PhMe_2SiCH_2)_3Sn$	−3.77 (151.7)[b] (26)	0.68 (51.5) (10.4)	141.26 (17.5)	133.20	128.79	127.64

[a] In $CDCl_3$; chemical shifts, δ, in ppm with respect to TMS; $^nJ(^{119}Sn,^{13}C)$ and $^1J(^{29}Si,^{13}C)$ coupling constants in Hz (in parentheses); nd = not determined. [b] $^2J(^{119}Sn,^{13}C)$: 48.7 Hz.

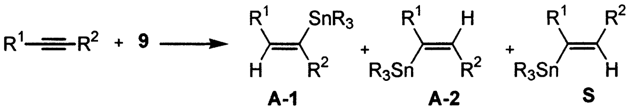
Table 3. ^{1}H, ^{119}Sn, and ^{29}Si NMR Data of Compounds 4, 5, 9, and 10[a]



compd no.	R	Z	^{1}H NMR chemical shifts (δ, in ppm)[a]	δ ^{119}Sn	δ ^{29}Si [$^2J(^{29}Si,^{119}Sn)$]
4	Cl	Cl	0.66 [s, 4H, ^2J(Sn,H) 95.9]; 0.41 (s, 12H); 7.39−7.48 (m, 10H)	134.92	−3.18 (31.6)
5	$PhMe_2SiCH_2$	$PhMe_2SiCH_2$	−0.11 [s, 8H, ^2J(Sn,H) 69.8]; 0.26 (s, 24H); 7.40−7.60 (m, 20H)	25.93	−2.18 (21.7)
9	$PhMe_2SiCH_2$	H	0.034 [s, 6H, ^2J(Sn,H) 73.3]; 0.34 (s, 18H); 7.20−7.50 (m, 15H)	−86.41	−2.25 (26.6)
10	$PhMe_2SiCH_2$	$(PhMe_2SiCH_2)_3Sn$	0.093 [s, 12H, ^2J(Sn,H) 62.3]; 0.21 (s, 36H); 7.28−7.40 (m, 30H)	−71.03 [b]	−2.91 (24.2)

[a] In $CDCl_3$; chemical shifts, δ, in ppm with respect to TMS (^{1}H and ^{29}Si spectra) and Me_4Sn (^{119}Sn spectra); coupling constants in Hz (in parentheses). [b] $^1J(^{119}Sn,^{119}Sn)$ = 3775.3 Hz.

Table 4. Tris[(phenyldimethylsilyl)methyl]tin Hydride Radical Additions to Substituted Alkynes



R = (Phenyldimethylsilyl)methyl = $PhMe_2SiCH_2$

compd no.	time (h)	temp (°C)	R^1	R^2	**A-2** (%)	**S** (%)	yield[b] (%)	^{119}Sn[c] (ppm)
11	6	85	H	Ph		100	72	−17.2
12	2	80	H	CH_2OH	100		98	−40.4
13	0.7	75	H	COOMe	100		98	−37.3
14	2.3	85	H	MeCHOH	100		69	−41.1
15	7	80	Ph	Ph		100	98	−27.3
16	1.5	65	CH_2OH	Me	100		98	−34.0
17	1	75	COOEt	Ph	100		98	−23.7

[a] The reactions were carried out under a nitrogen atmosphere; ratio hydride/alkyne = 1; AIBN 0.01 equiv; without solvent. [b] From the ^{119}Sn and ^{1}H NMR. [c] In $CDCl_3$.

A summary of the obtained results is shown in Table 4. This table also includes the best reaction conditions for these additions. It can be seen that in most cases only one of the two possible *Z anti* adducts (**A-2**) is obtained, while in two cases *E*-adducts are obtained (**S**).

Table 4 shows that the addition of hydride **9** to propargyl alcohol, methyl propiolate, 1-butyn-3-ol, diphenylethyne, 2-butyn-1-ol, and ethyl 3-phenylpropiolate leads exclusively to the *Z*-vinylstannanes resulting from an *anti* attack, typical of radical hydrostannations. In this table it can also be seen that in the additions to phenylethyne and diphenylethyne under radical conditions *E*-adducts were the sole products. The formation of the *E*-adducts from **11** and **15** could be explained by taking into account that the known isomerization of the initially formed kinetic *Z*-products by further addition/elimination of the stannyl radical would favor, under these reaction conditions (prolonged reaction times), the formation of the thermodynamically more stable *E*-vinylstannanes.[7,8]

The geometry assigned to compounds **12**−**14** and **16** and **17** follows from the large ^3J(Sn,H) coupling constants, mostly well over 120 Hz, that indicate the existence of *trans* H−C−C−Sn linkages in these compounds. The observed ^3J(Sn,H) coupling constants for compounds **11** and **15**, 81 and 84 Hz, respectively, clearly indicate the existence of a *cis* H−C−C−Sn

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

(8) Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1968**, *11*, 541.

linkage in these compounds. These structures were confirmed by other ^{1}H and ^{13}C NMR data.

The results obtained show that the additions of the new organotin hydride **9** to mono- and disubstituted alkynes under radical reaction conditions lead to vinylstannanes with both excellent stereoselectivity and even better yields than the recently reported additions of the bulky trineophyltin hydride to the same alkynes.[2f]

Further investigations on the properties of organotin reagents with phenyldimethylsilylmethyl ligands are in progress.

Experimental Section

NMR spectra were obtained using a Bruker ARX 300 instrument. Infrared spectra were recorded with a Nicolet Nexus FT spectrometer. Mass spectra were obtained using a Finnigan MAT Model 8230 at Dortmund University (Germany). Microanalyses were performed at Dortmund University. The refractive indices were measured with a Universal Abbe Zeiss Jena VEB instrument, and the melting points were determined in a Kofler hot stage and are uncorrected. Methyl(bromomethyl)chlorosilane[9] and (bromomethyl)phenyldimethylsilane (**1**)[10] were obtained following known procedures. All the solvents and reagents used were analytical reagent grade.

Synthesis of Tris[(phenyldimethylsilyl)methyl]tin Chloride (3) and Bis[(phenyldimethylsilyl)methyl]tin Dichloride (4). To magnesium turnings (0.53 g, 0.0239 mol) in dry diethyl ether (5 mL) under stirring was added slowly and dropwise a solution of (bromomethyl)phenyldimethylsilane (**1**) (4.97 g, 0.0217 mol) in diethyl ether (15 mL). The preparation was carried out under an atmosphere of nitrogen. The reaction was exothermic, and after the addition was completed the mixture was refluxed during 1 h. Then the reaction mixture was stirred for 15 h at room temperature. The solution of the Grignard reagent **2** thus obtained had a 1.24 M concentration.

To a solution of $SnCl_4$ (10.4 mL, 23 g, 0.088 mol) in dry toluene (200 mL) at 0 °C under nitrogen was added slowly and dropwise with stirring a solution of the Grignard reagent **2** in diethyl ether (0.264 mol, 213 mL of 1.24 M solution). The mixture was stirred for 1.5 h at room temperature, then refluxed for 3 h, and finally left 15 h at room temperature with stirring. After cooling at 0 °C, the reaction mixture was decomposed with a saturated solution of NH_4Cl (ca. 150 mL). The organic layer was separated, and the aqueous layer was extracted three times with diethyl ether (ca. 100 mL each). The combined organic extracts were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The ^{119}Sn NMR of the resulting oil (47.53 g) showed it to consist of a mixture of tris[(phenyldimethylsilyl)methyl]tin chloride (**3**) and bis[(phenyldimethylsilyl)methyl]tin dichloride (**4**) in a ratio **3**/**4** = 13.28:1 (47.53 g, 91% yield of organotin compounds based upon $SnCl_4$ used). This mixture was very soluble in solvents such as CH_2Cl_2, diethyl ether, cyclohexane, hexane, and petroleum ether at 30−60 °C. In the latter solvent even at low temperature (−23 °C) we were unable to obtain pure crystals of these compounds.

Synthesis of Hexakis[(phenyldimethylsilyl)methyl]distannoxane (6) and Tris[(phenyldimethylsilyl)methyl]tin Hydroxide (7). To a solution of the mixture of tin chlorides **3** and **4** in the ratio **3**/**4** = 13.28:1 (47.53 g) in diethyl ether (350 mL) was added a 10% aqueous solution of NaOH (50 mL), and the mixture was vigorously stirred during 3 h. The organic layer was decanted and treated again with the aqueous solution of NaOH. Then the organic layer was separated, washed three times with water, and dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the ^{119}Sn NMR spectrum of the liquid product showed it to consist of an equilibrium mixture of hydroxide **7** and oxide **8** (45.5 g, 98−99%), which was used without further purification for the synthesis of hydride **9**.

Synthesis of Tris[(phenyldimethylsilyl)methyl]tin Hydride (9). To a solution of the previous mixture of **7** and **8** (45.5 g) in dry tetrahydrofuran (200 mL) was added dropwise a solution of borane in THF (0.088 mol, 88 mL of a 1 M solution). The preparation was carried out under an atmosphere of nitrogen and with magnetic stirring. The mixture was refluxed during 1 h and the solvent distilled off under reduced pressure. Diethyl ether (100 mL) and water (5 mL) were then added. After 10 min stirring, the aqueous layer was decanted and the ether layer was dried over $MgSO_4$. The solution was filtered, and removal of the solvent under reduced pressure gave **9** as a liquid, μ_{D}^{25} 1.5674 (44.5 g, 0.0784 mol, 89% yield based upon $SnCl_4$ used initially). MS (*m*/*z*, rel int): 419 (100%, $[M - (CH_2Si(CH_3)_2Ph)]^+$, Sn-pattern); 418 (57%, $[M - H)]^+$, Sn-pattern); 299 (3%, $[HSnCH_2Si(CH_3)_2Ph)]^+$, Sn-pattern); 135 (76%, $[Si(CH_3)_2Ph]^+$; 119 (8%, $[Sn]^+$, Sn-pattern). IR (KBr, cm^{-1}): ν_{Sn-H} 1816. Anal. Calcd for $C_{27}H_{40}Si_3Sn$ (567.57): C, 57.13; H, 7.10. Found: C, 57.48; H, 7.24.

Synthesis of Hexakis[(phenyldimethylsilyl)methyl]distannane (10). To a solution of hydride **9** (0.38 g, 0.669 mmol) in dry benzene (1 mL) under an atmosphere of nitrogen and with magnetic stirring was added $Pd(PPh_3)_2Cl_2$ (0.116 g, 0.17 mmol), and the mixture was stirred 3 h at 40 °C. Then the solvent was distilled off under reduced pressure, and the crude product was purified by flash chromatography on silica gel 60, distannane **10** (0,28 g, 0.247 mmol, 74%) being eluted in the fraction cyclohexane/diethyl ether (99.3:0.7). Mp: 50−52 °C. MS (*m*/*z*, rel int): 567 (100%, $[M - Sn(CH_2Si(CH_3)_2Ph)_3]^+$, Sn-pattern); 417 (2%, $[Sn(CH_2Si(CH_3)_2Ph)_2]^+$, Sn-pattern); 357 (15%, $[(CH_2Si(CH_3)_2Ph)_2]^+$ Sn-pattern); 268 (18%, $[(SnCH_2Si(CH_3)_2Ph)]^+$ Sn-pattern); 135 (30%, $[Si(CH_3)_2Ph]^+$); 119 (2%, $[Sn]^+$, Sn-pattern). Anal. Calcd for $C_{54}H_{78}Si_6Sn_2$ (1133.10): C, 57.23; H, 6.94. Found: C, 57.36; H, 7.03.

Synthesis of Tetrakis[(phenyldimethylsilyl)methyl]stannane (5). To a solution of $SnCl_4$ (4 mL, 8.84 g, 0.0339 mol) in dry toluene (80 mL), under nitrogen, at room temperature was added slowly and dropwise with stirring a solution of the Grignard reagent **2** in diethyl ether (0.139 mol, 108 mL of 1.24 M solution). The mixture was stirred for 15 h at room temperature and then refluxed for 3 h. After cooling at 0 °C, the reaction mixture was decomposed with a saturated solution of NH_4Cl (ca. 50 mL). The organic layer was separated, and the aqueous layer was extracted three times with diethyl ether (ca. 50 mL each). The combined organic extracts were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. One recrystallization of the resulting oil from petroleum ether (30−60 °C) afforded **5** as a white crystalline solid (24.25 g, 0.0338 mol, 99%). Mp: 48−50 °C. MS (*m*/*z*, rel int): 567 (100%, $[M - (CH_2Si(CH_3)_2Ph)]^+$, Sn-pattern); 475 (68%, $[M - (CH_2Si(CH_3)_2Ph)]^+$, Sn-pattern); 267 (9%, $[(SnCH_2Si(CH_3)_2Ph)]^+$ Sn-pattern); 135 (30%, $[Si(CH_3)_2Ph]^+$); 119 (2%, $[Sn]^+$, Sn-pattern). Anal. Calcd for $C_{36}H_{52}Si_4Sn$ (715.87): C, 60.40; H, 7.32. Found: C, 60.49; H, 7.39.

Synthesis of Bis[(phenyldimethylsilyl)methyl]tin Dichloride (4). To a solution of $SnCl_4$ (5.2 mL, 11.5 g, 0.044 mol) in dry toluene (100 mL) at room temperature was added slowly and dropwise with stirring a solution of the Grignard reagent **2** in diethyl ether (0.264 mol, 213 mL of 1.24 M solution) under nitrogen. The mixture was left 15 h at room temperature and then refluxed for 3 h. After cooling at 0 °C, the reaction mixture was decomposed with a saturated solution of NH_4Cl (ca. 75 mL). The organic layer was separated, and the aqueous layer was extracted three times with diethyl ether (ca. 50 mL each). The combined organic extracts were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The ^{119}Sn NMR of the resulting oil showed

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[9] Carleer, R.; Anteunis, M. J. O. *Org. Magn. Reson.* **1980**, *13*, 253.

[10] Farbenfabriken Bayer, A.-G. Ger. Pat. 1,242,615 (Cl. C 07f); *Chem. Abstr.* **1967**, *67*, 90931q.

it to consist of a mixture of tris[(phenyldimethylsilyl)methyl]-tin chloride (**3**), bis[(phenyldimethylsilyl)methyl]tin dichloride (**4**), and tetrakis[(phenyldimethylsilyl)methyl]tin (**5**) in a ratio **3**/**4**/**5** = 1.14:6.98:1 (18.8 g, 81% yield of organotin compounds based upon $SnCl_4$ used). From this mixture and after repeated recrystallizations in *n*-heptane we were able to obtain **4** pure (4.56 g, 0.0093 mol, 21%).

Hydrostannation of Substituted Alkynes. All the reactions were carried out following the same procedure. One experiment is described in detail in order to illustrate the methods used.

Addition of Tris[(phenyldimethylsilyl)methyl]tin Hydride (9): Synthesis of Methyl (*Z*)-3-[(Tris(phenyldimethylsilyl)methyl)stannyl]propenoate (13). Methyl propiolate (0.15 g, 1.78 mmol) was treated for 0.7 h with hydride **9** (1.01 g, 1.78 mmol) under nitrogen at 75 °C and with AIBN as a catalyst (this optimal time of reaction was indicated by earlier experiments in which the reaction was monitored by taking samples at intervals and observing the disappearance of the Sn−H absorption by IR). The ^{1}H, ^{13}C, and ^{119}Sn NMR spectrum of the crude product showed that it consisted of isomer *Z*-**13** only. We found that, unlike trineophyltin adducts,[2f] most of these adducts tend to decompose in silica gel, bringing the yields of isolated products down to 41−57%. Therefore, for other studies we used adducts **11**−**17** without further purification.

Acknowledgment. This work was supported by CONICET (Capital Federal, Argentina) and Universidad Nacional del Sur (Bahía Blanca, Argentina). We acknowledge a research grant from Fundación Antorchas (Argentina). Fellowships from the DAAD (Germany) and CONICET to one of us (V.I.D.) are also gratefully acknowledged.

Supporting Information Available: Mass spectra and the ^{1}H as well as ^{13}C NMR characteristics of the new adducts thus obtained are available as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020936B