A General Route to Alkylene-, Arylene-, or Benzylene-Bridged Ditin Hexachlorides and Hexaalkynides

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The preparation of alkylene-, arylene-, or benzylene-bridged ditin hexachlorides in high yields from the reaction of the corresponding hexacyclohexylated compounds with tin tetrachloride is described. The tetragonal geometry of the tin atom of 1,4-bis(trichlorostannyl)-butane in the solid state indicates that no intramolecular or intermolecular interaction involving either end of the molecule exists in this compound. The ditin hexachlorides were successfully transformed in the corresponding hexaalkynides, precursors of hybrid materials.

Since they were first described in 1957,[1,2] distannylated derivatives have received much attention. 1,2-Hexaorganodistannylated compounds have interesting applications in the Stille reaction,[3] while 1,*n*-haloorganodistannylated species have been mainly studied as Lewis acids due to their ability to complex anions.[4] Several methods of preparation have been described, depending on the nature of the linker between the metal atoms. When the two tins are separated by an alkyl or alkenyl chain, they can be incorporated either at the same time or successively. In the first case, the more straightforward way involves either the coupling of a triorganostannylmetal with a dihalide[5] or the coupling of a di-Grignard or a dilithium reagent with a triorganotin halide.[6] Bis(stannyl)acetylenes can be prepared from a triorganotin halide and CaC_2 with ultrasound.[7] However, when these dimetallic species are not available, the palladium-catalyzed[8] or noncatalyzed[9] addition of a hexaorganoditin to unsaturated compounds can be successfully performed. The second case mainly involves the hydrostannation of an unsaturated tetraorganotin compound.[2] When the two tins are separated by an aryl ring, it is possible to use a cycloaddition reaction,[10] the coupling of a di-Grignard or a dilithium reagent with an triorganotin halide,[11] or a triorganostannylmetal with an aryl halide.[12] Then classical electrophilic reactions allow facile transformation to the corresponding oxides or halides. However, the described preparations are limited to distannylalkyl derivatives where the strong tin−alkyl bonds allow the linkage between both tins to be preserved.

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[1] Zimmer, H.; Mosle, H.-G. *Chem. Ber.* **1954**, *87*, 1255.

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

[3] Farina, V.; Krishnamurphy, V.; Scott, W. J. In *The Stille Reaction*; Wiley: New York, 1998. Jousseaume, B.; Pereyre. In *The Chemistry of Tin*, 2nd ed. Smith, P., Ed.; Blackie: London, 1998; p 290.

[4] (a) Swami, K.; Hutchinson, J. P.; Kuivila, H. G.; Zubieta, J. A. *Organometallics* **1984**, *3*, 1687. (b) Hyde, J. R.; Karol, T. J.; Hutchinson, J. P.; Kuivila, H. G.; Zubieta, J. A. *Organometallics* **1982**, *1*, 404. (c) Karol, T. J.; Hutchinson, J. P.; Hyde, J. R.; Kuivila, H. G.; Zubieta, J. A. *Organometallics* **1983**, *2*, 106. (d) Kuivila, H. G.; Karol, T. J.; Swami, K. *Organometallics* **1983**, *2*, 909. (e) Austin, M.; Gebreyes, K.; Kuivila, H. G.; Swami, K.; Zubieta, J. A. *Organometallics* **1987**, *6*, 834. (f) Gielen, M.; Jurkschat, K.; Meunier-Piret, J.; van Meerssche, M. *Bull. Soc. Chim. Belg.* **1984**, *93*, 379. (g) Meunier-Piret, J.; van Meerssche, M.; Jurkschat, K.; Gielen, M. *J. Organomet. Chem.* **1985**, *288*, 139. (h) Jurkschat, K.; Hesselbarth, F.; Dargatz, M.; Lehmann, J.; Kleinpeter, E.; Tzschach, A.; Meunier-Piret, J. *J. Organomet. Chem.* **1990**, *388*, 259. (i) Chaniotakis, N. A.; Jurkschat, K.; Rühlemann, A. *Anal. Chim. Acta* **1993**, *282*, 345. (j) Tsagatakis, J. K.; Chaniotakis, N. A.; Jurkschat, K. *Helv. Chim. Acta* **1994**, *77*, 2191. (k) Dakternieks, D.; Jurkschat, K.; Zhu, H.; Tiekink, E. R. T. *Organometallics* **1995**, *14*, 2512. (l) Altmann, R.; Schürmann, M.; Jurkschat, K.; Dakternieks, D.; Duthie, A. *Organometallics* **1997**, *16*, 5716. (m) Newcomb, M.; Horner, J. H.; Blanda, M. T.; Squattrito, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 6294. (n) Blanda, M. T.; Newcomb, M. *Tetrahedron Lett.* **1989**, *30*, 3501. (o) Horner, J. H.; Squattrito, P. J.; McGuire, N.; Riebenspies, J. P.; Newcomb, M. *Organometallics* **1991**, *10*, 1741. (p) Jurkschat, K.; Kuivila, H. G.; Liu, S.; Zubieta, J. A. *Organometallics* **1989**, *8*, 2755. (q) Jurkschat, K.; Rühlemann, A.; Tzschach, A. *J. Organomet. Chem.* **1990**, *381*, C53. (r) Altmann, R.; Jurkschat, K.; Schürmann, M.; Dakternieks, D.; Duthie, A. *Organometallics* **1998**, *17*, 5858. (s) Zobel, B.; Duthie, A.; Dakternieks, D.; Tiekink, E. R. T. *Organometallics* **2001**, *20*, 2820. (t) Zobel, B.; Duthie, A.; Dakternieks, D.; Tiekink, E. R. T. *Organometallics* **2001,** *20,* 3347.

[5] Traylor, T. G.; Koermer, G. S. *J. Org. Chem.* **1981**, *46*, 3651.

[6] Bulten, E. J.; Budding, H. A. *J. Organomet. Chem.* **1976**, *110*, 167.

[7] Cochran, J. C.; Lemieux, R. P.; Giacobbe, R. C.; Roitstein, A. *Synth-React. Inorg. Met.-Org. Chem.* **1990**, *20*, 251.

[8] Mitchell, T. M.; Amamria, A.; Killing, H.; Rutshow, D. *J. Organomet. Chem.* **1986**, *304*, 257.

[9] Beg, M. A. A.; Clark, H. C. *Chem. Ind.* **1962**, 140.

[10] Evnin, A. B.; Seyferth, D. *J. Am. Chem. Soc.* **1967**, *89*, 952.

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We have been interested recently in the preparation of organotin precursors of hybrid materials,[13] which allowed us to present a new route to functional monoorganotins.[14] To broaden the scope of the avaliable precursors, as the corresponding disilylated compounds revealed excellent precursors of various types of microporous or mesoporous silica,[15] monoorganodistannylated compounds were needed. The classical method of preparation involving the electrophilic cleavage of phenyl groups in α,ω-bis(triphenyltin)alkanes has been very successfully applied for the preparation of alkylene-bridged ditin chlorides, studied due to their strong ability to form chelate complexes with anions. It cannot be applied to an aryl- or a benzyl-type linker, where the electrophilic cleavage would not be selective enough and would also cleave tin−bridge bonds, which would greatly reduce the yields. Here we present a general route to alkylene-, arylene-, or benzylene-bridged ditin compounds based on the use of auxiliary cyclohexyl groups. The first crystal structure of an uncomplexed polymethylene-bridged ditin hexachloride is also reported.

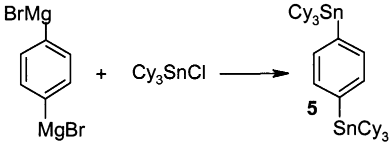
Results and Discussion

To prepare hydrolyzable alkylene-, arylene-, or benzylene-bridged hexaalkynylditins, precursors of hybrid alkylene-, arylene-, or benzylene-bridged tin oxide materials, it is necessary to have the corresponding hexachlorides. To obtain these species, the successful preparation of functional organotin trichlorides from the electrophilic reaction of the corresponding tricyclohexylorganotin with tin tetrachloride was used. A series of α,ω-dibromoalkanes was subjected to the reaction with an excess of magnesium, and then, a solution of tricyclohexyltin chloride was added. That allowed the isolation of alkylene-bridged hexacyclohexylditins in good yields with four, five, six, or ten methylene groups between the metals.

$$\mathrm{ClMg\text{-}(CH_2)_n\text{-}MgCl} + 2\ \mathrm{Cy_3SnCl} \longrightarrow \mathrm{Cy_3Sn\text{-}(CH_2)_n\text{-}SnCy_3}$$

1, n = 4; **2**, n = 5; **3**, n = 6, **4**, n = 10

This reaction was successfully extended to the preparation of phenylene-bridged hexacylohexylditins, as 1,4-bis(tricyclohexylstannyl)benzene (**5**) was isolated in 65% yield.



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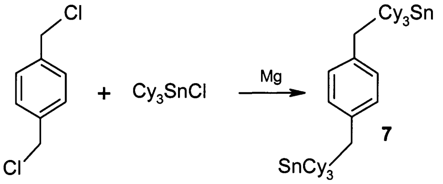
In the case of benzylene-bridged ditins, the method described above was only suitable for 1,2-disubstituted compounds, where the corresponding di-Grignard reagent is available. For the 1,4-disubstituted compound, a Barbier-type reaction was more appropriate, as the corresponding di-Grignard reagent is not very stable.



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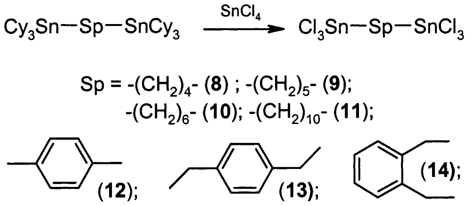
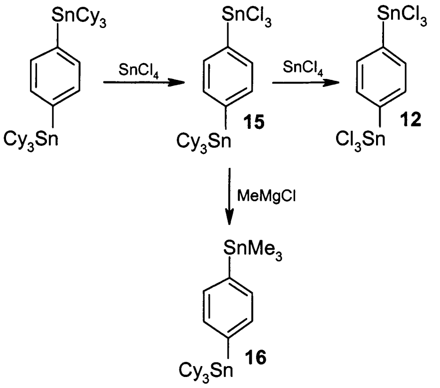
Subsequent treatment of these distannylated with tin tetrachloride afforded the corresponding hexachlorides in good yields. In the case of benzylic halides, the reaction had to be conducted at lower temperature to obtain good yields.



With 1,4-bis(tricyclohexylstannyl)benzene the reaction was slower than with other compounds and occurred stepwise. It was thus possible to isolate a mixed compound, 1-(trichlorostannyl)-4-(tricyclohexylstannyl)benzene, **15**, characterized by ^{119}Sn NMR spectroscopy by two peaks at −61.1 and −102.0 ppm, corresponding to the trichlorostannyl and to the tricyclohexylstannyl moiety, respectively. Alkylation with methylmagnesium chloride afforded 1-(tricyclohexylstannyl)-4-(trimethylstannyl)benzene, **16**, confirming the presence of an unsymmetrical compound.



The lower reactivity of the mixed compound was explained by a deactivation of the phenyl−tricyclohexylstannyl bond toward the electrophilic cleavage of tin

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[11] Boue, S.; Gielen, M.; Nasielski, J. *Bull. Soc. Chim. Belg.* **1967**, *76*, 559. Juara, K. L.; Hundal, H. S.; Handa, R. D. *Indian J. Chem.* **1967**, *5*, 211.

[12] Wursthorn, K. R.; Kuivila, H. G.; Smith, G. F. *J. Am. Chem. Soc.* **1977**, *100*, 2779.

[13] Ribot, F.; Banse, F.; Sanchez, C.; Lahcini, M.; Jousseaume, B. *J. Sol-Gel Sci. Technol.* **1997**, *8*, 529. Angiolini, L.; Caretti, D.; Carlini, C.; Jordens, F.; Jousseaume, B.; Niesel, T. *J. Inorg. Organomet. Polym.* **1998**, *8*, 48. Jaumier, P. Jousseaume, B.; Riague, H.; Toupance, T.; Lahcini, M. In *Hybrid Organic/Inorganic Materials*; Laine, R. M., Sanchez, C., Giannelis, E., Brinker, C. J., Eds.; MRS, 2000; Vol. 628, p CC12.

[14] Jousseaume, B.; Lahcini, M.; Rascle, M.-C.; Sanchez, C.; Ribot, F. *Organometallics* **1995**, *14*, 685. Jousseaume, B.; Lahcini, M.; Fouquet, E.; Barbe, B. *J. Org. Chem.* **1994**, *59*, 8292. Biesemans, M.; Willem, R.; Damoun, S.; Geerlings, P.; Lahcini, M.; Jaumier, P.; Jousseaume, B. *Organometallics* **1996**, *15*, 2237. Jaumier, P.; Jousseaume, B.; Tiekink, E. R. T. Biesemans, M.; Willem, R. *Organometallics* **1997**, *16*, 5124. Biesemans, M.; Willem, R.; Damoun, S.; Geerlings, P.; Tiekink, E. R. T.; Lahcini, M.; Jaumier, P.; Jousseaume, B. *Organometallics* **1998**, *17*, 90. Jaumier, P. Jousseaume, B.; Lahcini, M.; Ribot, F.; Sanchez, C. *J. Chem. Soc., Chem. Commun.* **1998**, 369. Jaumier, P.; Jousseaume, B. *Main Group Met. Chem.* **1998**, *21*, 325. Lahcini, M.; Jaumier, P.; Jousseaume, B. *Angew. Chem., Int. Ed.* **1999**, *32*, 402. Willem, R.; Biesemans, M.; Jaumier, P.; Jousseaume, B. *J. Organomet. Chem.* **1999**, *572*, 233.

Table 1. Selected Interatomic (Å, deg) Parameters for [$Cl_3Sn(CH_2)_4SnCl_3$][a]

Sn(1)−Cl(1)	2.289(2) [2.376(2)]	Cl(2)−Sn(1)−Cl(3)	104.88(9) [101.5(1)]
Sn(1)−Cl(2)	2.417(3) [2.236(3)]	Cl(1)−Sn(1)−C(1)	112.2(1) [114.8(1)]
Sn(1)−Cl(3)	2.3106(11)	Cl(2)−Sn(1)−C(1)	115.35(11) [127.19(11)]
Sn(1)−C(1)	2.128(3)	Cl(3)−Sn(1)−C(1)	110.32(8)
C(1)−C(2)	1.514(4)	Sn(1)−C(1)−C(2)	111.4(2)
C(2)−C(2A)	1.534(5)	C(1)−C(2)−C(2A)	111.0(3)
Sn(2)−Cl(4)	2.3009(9)	Cl(4)−Sn(2)−Cl(5)	110.17(9) [97.79(8)]
Sn(2)−Cl(5)	2.402(4) [2.272(4)]	Cl(4)−Sn(2)−Cl(6)	103.17(3)
Sn(2)−Cl(6)	2.3260(7)	Cl(5)−Sn(2)−Cl(6)	97.50(9) [104.1(1)]
Sn(2)−C(3)	2.132(3)	Cl(4)−Sn(2)−C(3)	122.65(8)
C(3)−C(4)	1.520(4)	Cl(5)−Sn(2)−C(3)	107.94(12)
C(4)−C(4B)	1.535(5)	Cl(6)−Sn(2)−C(3)	112.50(8)
		Sn(2)−C(3)−C(4)	110.5(2)
Cl(1)−Sn(1)−Cl(2)	101.16(12) [104.7(1)]	C(3)−C(4)−C(4B)	110.1(3)
Cl(1)−Sn(1)−Cl(3)	112.49(9) [91.90(8)]		

[a] Where relevant, the corresponding values for the other distorted component (i.e., Cl(11), Cl(21), and Cl(51) for atoms Cl(1), Cl(2), and Cl(5), respectively) are given in square brackets.

tetrachloride by the electron-withdrawing trichlorostannyl group situated in para position. A longer reaction time or moderate heating of the reaction mixture ensured the transformation of the remaining tricyclohexylstannyl group into the trichlorostannyl group. This electronegative effect was expressed in the strong coordination of the tins by acetonitrile, used in the acetonitrile/pentane extraction method, which could not be removed totally under vacuum. However, displacement of acetonitrile with a large excess of THF followed by evaporation of THF led to the unsolvated hexachloride. The same phenomenon occurred with 1,2- and 1,4-bis(trichlorostannylmethyl)benzene. An extra washing with THF was necessary to displace the acetonitrile, unsuitable for the next alkynylation with alkynyllithiums.

The question arose about an eventual internal coordination of the tins by chlorine atoms. To maximize the possible effects,[16] 1,4-bis(trichlorostannyl)butane, a compound susceptible to form the smallest rings by intramolecular coordination, which induces the stronger coordination, was chosen to be studied by X-ray crystallography. This is the first crystallographic structure of free hexachlorodistannylated compounds, known stuctures recently described being chloride,[4t] DMSO,[17] or water[4s,18] adducts. The atomic arrangements and the crystallographic numbering are shown in Figure 1. Selected interatomic parameters are listed in Table 1. The molecules lie across crystallographic inversion centers, and the asymmetric unit contains two halves of two independent molecules. Three of the chlorine atoms were disordered, which precludes any discussion about the geometry of the tin (for further details, see the Supporting Information). Nevertheless, it is clear that both of the tin centers are tetracoordinated, as in uncoordinated trichloroorganotins, and do not interact with each other by bridging chlorine atoms. The shortest intermolecular tin−chlorine distance (5.17 Å) is well outside the appropriate sum of their van der Waals radii (3.97 Å). The butylene group is not extended, as seen in the expanded angles subtended at each CH_2CH_2Sn carbon of 111.0(3)° and 110.1(3)° instead of ca. 114° in 1,4-bis(trichlorostannyl)butane, 2 benzyltriphenylphosphonium chloride.[4t]

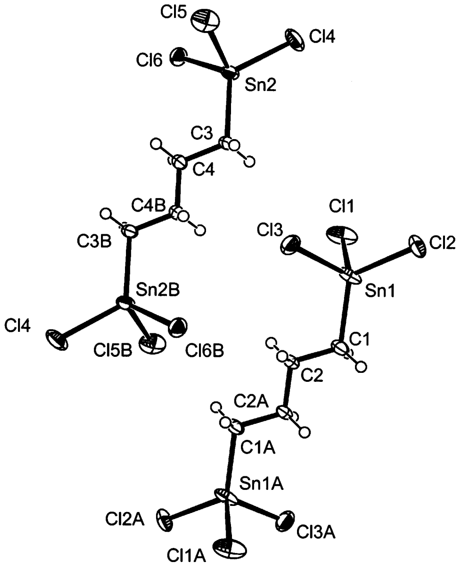
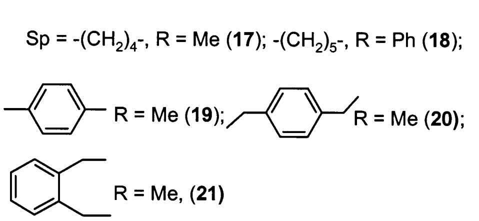


Figure 1. Molecular structure of $Cl_3Sn(CH_2)_4SnCl_3$.

Then alkynylation of the hexachlorides with propynyllithium or phenylethynyllithium gave the corresponding alkynides in good yields. To the best of our knowledge, ditin hexaalkynides are described here for the first time They were subsequently hydrolyzed in THF to give transparent or opaque gels, depending on the nature of



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(15) Shea, K. J.; Loy, D. A. *Chem. Mater.* **2001**, *13*, 3306. Shea, K. J.; Loy, D. A. *Acc. Chem. Res.* **2001**, *34*, 707. Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95*, 1431. Cerveau, G.; Corriu, R. J. P.; Framery, E. *Chem. Mater.* **2001,** *13,* 3373. Corriu, R. J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 1376.

(16) Jousseaume, B.; Villeneuve, P. *J. Chem. Soc., Chem. Commun.* **1987**, 517. Jousseaume, B.; Villeneuve, P.; Draeger, M.; Roller, S.; Chezeau, J. M. *J. Organomet. Chem.* **1988**, *349*, C1. Biesemans, M.; Willem, R.; Damoun, S.; Geerlings, P.; Lahcini, M.; Jaumier, P.; Jousseaume, B. *Organometallics* **1996**, *15*, 2237. Jaumier, P.; Jousseaume, B.; Tiekink, E. R. T. Biesemans, M.; Willem, R. *Organometallics* **1997**, *16*, 5124. Biesemans, M.; Willem, R.; Damoun, S.; Geerlings, P.; Tiekink, E. R. T.; Lahcini, M.; Jaumier, P.; Jousseaume, B. *Organometallics* **1998**, *17*, 90.

(17) Dakternieks, D.; Zobel, B.; Tiekink, E. R. T. *Main Group Met. Chem.* **2000**, *23*, 253.

(18) Dakternieks, D.; Zobel, B.; Tiekink, E. R. T. *Main Group Met. Chem.* **2000**, *23*, 321.

Table 2. Crystal Data and Structure Refinement for [$Cl_3Sn(CH_2)_4SnCl_3$]

empirical formula	$C_4H_8Cl_6Sn_2$
fw	506.21
cryst description	colorless block
cryst size, mm	0.30 × 0.20 × 0.20
temperature, K	150
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	7.7894(2)
b, Å	7.9828(2)
c, Å	11.7951(2)
α, deg	98.027(1)
β, deg	105.393(1)
γ, deg	98.9022(8)
V, Å	685.92(3)
Z	2
D_{calc}, g cm^{-1}	2.45
F(000)	466.15
μ, mm^{-1}	4.76
θ, deg	2.91−27.48
index ranges	$-10 \leq h \leq 9$ $-10 \leq k \leq 10$ $0 \leq l \leq 15$
no. of data colld	5741
no. of unique data with $I = 3.0\sigma(I)$	2728
R	0.026
R_w	0.025

the spacer, which were then thermolyzed, furnishing high surface area mesoporous tin oxide.[19]

Conclusion

It has been shown that alkylene-, arylene-, or benzylene-bridged hexacyclohexylditins react with tin tetrachloride under mild conditions to give the corresponding hexachlorides in quantitative yields. The strong tin−cyclohexyl bond makes the tricyclohexyltin group very useful in this case, allowing the facile preparation of ditin hexachlorides with fragile tin−phenyl or tin−benzyl bonds. The crystal structure of 1,4-bis(trichlorostannyl)butane revealed that no interaction exists between the two trichlorotin groups. Applications of the corresponding hexaalkynides to the preparation of mesoporous tin oxide are in progress.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Pentane, THF, and diethyl ether were distilled from sodium benzophenone ketyl prior use. Acetonitrile was distilled over CaH_2. Tin tetrachloride was distilled before use. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-250 spectrometer (solvent $CDCl_3$), and ^{119}Sn NMR spectra were recorded on a Bruker DPX-200 spectrometer (solvent $CDCl_3$). Tin−hydrogen and tin−carbon coupling constants are given in square brackets.

General Procedure for the Preparation of Bis(tricyclohexylstannyl)alkyl and -aryl Derivatives. A solution of alkyl or aryl dibromide (59 mmol) in THF (80 mL) was slowly added to magnesium (3.0 g, 125 mmol) in THF (10 mL). The mixture was refluxed for 30 min and cooled at room temperature, and a solution of triclohexyltin chloride (39.43 g, 97.8 mmol) in THF (150 mL) was added. After refluxing for 1 h the mixture was hydrolyzed with a saturated solution of NH_4Cl, extracted with petroleum ether (100 mL), and dried with $MgSO_4$, and the solvents were evaporated. Recrystallization from petroleum ether gave the pure products.

1,4-Bis(tricyclohexylstannyl)butane, 1: mp 235 °C; 71% yield; ^1H δ 0.7−0.9 (m, 4H); 1.1−2.0 (m, 70H). ^{13}C δ 7.1 [276]; 26.3 [320]; 27.5 [7]; 29.8 [52]; 32.8 [16]; 33.3; ^{119}Sn δ −64.9. Anal. Calcd for $C_{40}H_{74}Sn_2$: C, 60.63; H, 9.41; Sn, 29.96. Found: C, 60.63; H, 9.41; Sn, 29.96.

1,5-Bis(tricyclohexylstannyl)pentane, 2: mp 150 °C; 61% yield; ^1H δ 0.70−0.90 (m, 4H); 1.10−1.95 (m, 72H); ^{13}C δ 6.9 [269]; 26.3 [320]; 26.9 [20]; 27.7 [11]; 29.7 [51]; 32.8 [15]; 40.4 [48]; ^{119}Sn δ −65.2. Anal. Calcd for $C_{41}H_{76}Sn_2$: C, 61.07; H, 9.50; Sn, 29.44. Found: C, 60.83; H, 9.59; Sn, 28.41.

1,6-Bis(tricyclohexylstannyl)hexane, 3: mp 157 °C; 58% yield; ^1H δ 0.6−1.0 (m, 4H); 1.1−2.0 (m, 74H); ^{13}C δ 7.0; 25.9 [308]; 27.4 [15]; 29.4 [62]; 32.2; 32.5 [21]; 34.6; ^{119}Sn δ −65.3. Anal. Calcd for $C_{42}H_{78}Sn_2$: C, 61.49; H, 9.58; Sn, 28.93. Found: C, 61.11; H, 9.48; Sn, 29.06.

1,10-Bis(tricyclohexylstannyl)decane, 4: mp 182 °C; 61% yield; ^1H δ 0.7−0.9 (m, 4H); 1.1−2.0 (m, 82H); ^{13}C δ 7.0; 26.0 [317]; 27.5 [8]; 29.1 [5]; 29.5 [53]; 29.9; 32.6 [16]; 35.5; 40.1; ^{119}Sn δ −65.8. Anal. Calcd for $C_{46}H_{86}Sn_2$: C, 63.03; H, 9.89; Sn, 27.08. Found: C, 63.54; H, 9.74; Sn, 27.62.

1,4-Bis(tricyclohexylstannyl)benzene, 5: mp 125 °C; 65% yield; ^1H δ 1.1−1.9 (m, 66H); 8.07 (s, 4H, [29]); ^{13}C δ 25.5 [320]; 27.6; 29.9 [60]; 33.0 [18]; 137.8; 141.0; ^{119}Sn δ −104.4. Anal. Calcd for $C_{42}H_{70}Sn_2$: C, 62.10; H, 8.69; Sn, 29.22. Found: C, 62.85; H, 8.94; Sn, 28.35.

1,2-Bis(tricyclohexylstannylmethyl)benzene, 6. The Grignard reagent was prepared from the corresponding dichloride: mp 129 °C; 69% yield; ^1H δ 1.1−1.9 (m, 66H); 2.3 (s, 4H, [52]); 6.80−6.95 (m, 4H); ^{13}C δ 14.4 [214]; 27.3 [304]; 27.4; 29.5 [55]; 32.3 [16]; 123.2; 127.9; 139.0; ^{119}Sn δ −75.9 [60]. Anal. Calcd for $C_{44}H_{74}Sn_2$: C, 62.88; H, 8.87; Sn, 28.24. Found: C, 62.71; H, 8.92; Sn, 28.63.

1,4-Bis(tricyclohexylstannylmethyl)benzene, 7. In this case, a solution of 9.45 g (54 mmol) of 1,4-bis(chloromethyl)benzene and 40 g (99 mmol) of tricyclohexylchloroethane in THF (175 mL) was slowly added to magnesium (5.2 g, 214 mmol) and THF (250 mL): mp 117 °C; 78% yield; ^1H δ 1.1−1.9 (m, 66H); 2.2 (s, 4H [56]); 6.85 (s, 4H); ^{13}C δ 14.9 [209]; 26.8 [318]; 27.4; 29.4 [55]; 32.5 [16]; 127.4 [19]; 137.8; ^{119}Sn δ −76.29 [58]. Anal. Calcd for $C_{44}H_{74}Sn_2$: C, 62.88; H, 8.87; Sn, 28.24. Found: C, 62.29; H, 8.85; Sn, 29.40.

General Procedure for the Preparation of Bis(trichlorostannyl)alkyl and -aryl Derivatives. $SnCl_4$ (8.8 mL, 75 mmol) was slowly added to a solution of bis(tricyclohexylstannylated) compound (29 mmol) in toluene (60 mL). After stirring at 70 °C for 15 h, the solvent was evaporated under reduced pressure. Acetonitrile (50 mL) was added. The solution was extracted with petroleum ether (5 × 20 mL) to remove tricyclohexyltin chloride. Acetonitrile was evaporated to give the pure hexachloride.

1,4-Bis(trichlorostannyl)butane,[4s] **8:** mp 58 °C; 94% yield; ^1H δ 2.45 (m, 4H); 2.73(m, 4H); ^{13}C δ 27.6 [55, 141]; 31-[8, 700]; ^{119}Sn δ 5.1.

1,5-Bis(trichlorostannyl)pentane,[4s] **9:** viscous liquid; 93% yield; ^1H δ 1.67 (m, 2H); 2.02 (quint, 4H); 2.42 (t, 4H, [85]); ^{13}C δ 24.4 [58]; 32.4 [662]; 34.8 [126]; ^{119}Sn δ 4.0.

1,6-Bis(trichlorostannyl)hexane, 10: viscous liquid; 97% yield; ^1H δ 1.94 (m, 4H); 2.33 (m, 4H); 2.75 (m, 4H, [86]); ^{13}C δ 24.8 [57]; 31.9 [111]; 32.8 [659]; ^{119}Sn δ 3.0. Anal. Calcd for $C_6H_{12}Cl_6Sn_2$: C, 13.49; H, 2.26; Sn, 44.43. Found: C, 14.14; H, 2.61; Sn, 45.24.

1,10-Bis(trichlorostannyl)decane, 11: viscous liquid; 98% yield; ^1H δ 1.2−1.6 (m, 12H); 1.85−2.05 (m, 4H); 2.42 (t, 4H); ^{13}C δ 25.0 [78]; 29.2; 29.5; 32.9 [135]; 33.8 [807]; ^{119}Sn δ 5.9. Anal. Calcd for $C_{10}H_{20}Cl_6Sn_2$: C, 20.35; H, 3.41; Sn, 40.21. Found: C, 19.81; H, 3.87; Sn, 41.15.

1,4-Bis(trichlorostannyl)benzene, 12. The poor solubility of the hexachloride required the use of 200 mL of acetonitrile. The solid was solubilized in THF, and the solvent evaporated: mp 135 °C; 95% yield; ^1H δ 7.80 (s, 4H [55, 130]); ^{13}C δ 118.0 [60, 110]; 136.0; ^{119}Sn δ −66.3. Anal. Calcd for C_6H_4-

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(19) Jousseaume, B.; Riague, E.; Toupance, T. To be published.

Cl_6Sn_2: C, 13.70; H, 0.77; Sn, 45.11. Found: C, 14.54; H, 1.03; Sn, 45.91. Anal. Calcd for $C_8H_8Cl_6Sn_2$: C, 17.34; H, 1.45; Sn, 42.83. Found: C, 17.75; H, 1.63; Sn, 42.07.

1,2-Bis(trichlorostannylmethyl)benzene, 13. The addition of tin tetrachloride was conducted at −30 °C: mp 86 °C; 90% yield; ^1H δ 4.68 (s, 4H, [116]); 8.28 (m, 4H); ^{13}C δ 44.8; 136.5; 148.6; 151.0; ^{119}Sn δ −62.2. Anal. Calcd for $C_8H_8Cl_6Sn_2$: C, 17.34; H, 1.45; Sn, 42.83. Found: C, 17.75; H, 1.63; Sn, 42.07.

1,4-Bis(trichlorostannylmethyl)benzene, 14. The addition of tin tetrachloride was conducted at −30 °C. Recrystallized from THF/CH_2Cl_2: mp 73 °C; 89% yield; ^1H δ 4.05 (s, 4H, [20, 115]); 7.65 (s, 4H); ^{13}C δ 40.9; 150.0; 153.1; ^{119}Sn δ −33.7. Anal. Calcd for $C_8H_8Cl_6Sn_2$: C, 17.34; H, 1.45; Sn, 42.83. Found: C, 16.61; H, 1.29; Sn, 41.13.

1-(Trichlorostannyl)-4-(tricyclohexylstannyl)benzene, 15. The addition of 1 equiv of tin tetrachloride was conducted at −30 °C. After extraction with toluene the compound was recovered as a solid contaminated with some tricyclohexyltin chloride: ^1H δ 1.1−1.9 (m, 33H); 7.42 (m, 4H); ^{13}C δ 27.4; 27.6; 29.7; 32.7; 127.8; 135.1; 136.8; 147.3; ^{119}Sn δ −61.1; −102.0.

1-(Tricyclohexylstannyl)-4-(trimethylstannyl)benzene, 16. To a solution of crude **12** (6.69 g, 10 mmol) in THF at 0 °C was added a solution of MeMgI (60 mmol) in diethyl ether. After stirring for 2 h at room temperature, the solution was hydrolyzed and dried, the solvents were evaporated, and **16** was recovered as an oil after chromatography on silica gel: 84% yield; ^1H δ 0.47 (s, 9H), 1.1−1.9 (m, 33H); 7.94 (m, 4H); ^{13}C δ −9.5; 26.6; 27.5; 29.6; 32.8; 135.1; 137.5; 141.3; 141.9; ^{119}Sn δ −29.6; −104.4. Anal. Calcd for $C_{27}H_{46}Sn_2$: C, 53.33; H, 7.63; Sn, 39.04. Found: C, 53.87; H, 7.95; Sn, 38.43.

General Procedure for the Preparation of Bis(trialkynylstannyl)alkyl and -aryl Derivatives. To a solution of phenylacetylene (22.85 g, 224 mmol) (or propyne, 400 mmol) in toluene (50 mL) at −78 °C was slowly added a solution of butyllithium in hexanes (81.6 mL, 204 mmol). After 15 min stirring at room temperature, a solution of 1,5-bis(trichlorostannyl)pentane (14.6 g, 28 mmol) in toluene (60 mL) was added at −78 °C. The suspension was then heated at 70 °C for 12 h. The suspension was filtered on dry $MgSO_4$ under dry N_2 and the toluene evaporated. The solids were recrystallized from toluene.

1,4-Bis(triprop-1-ynylstannyl)butane, 17: mp 95 °C; 59% yield; ^1H δ 1.54 (t, 4H [78]); 2.04 (m, 4H); 2.21 (s, 18H [15]); ^{13}C δ 5.6 [16]; 14.6 [650]; 29.0 [30, 94]; 76.9 [810]; 108.1 [168]; ^{119}Sn δ −252 [30]. Anal. Calcd for $C_{22}H_{26}Sn_2$: C, 50.06; H, 4.97; Sn, 44.97. Found: C, 49.33; H, 4.90; Sn, 46.18.

1,5-Bis(tris(phenylethynyl)stannyl)pentane, 18: mp 127 °C; 79% yield; ^1H δ 1.64 (t, 4H); 1.80 (m, 4H); 2.00 (quint, 4H); 7.35 (m, 12H); 7.59 (m, 6H); ^{13}C δ 15.9 [788]; 25.1 [40]; 36.4 [116]; 87.5 [900]; 110.3 [204]; 122.7 [22]; 128.4; 129.0; 132.4 [13]; ^{119}Sn δ −242.1. Anal. Calcd for $C_{53}H_{40}Sn_2$: C, 69.63; H, 4.41; Sn, 25.96. Found: C, 68.07; H, 4.33; Sn, 26.31.

1,4-Bis(triprop-1-ynylstannyl)benzene, 19: mp >250 °C; 47% yield; ^1H δ 1.85 (s, 18H); 7.62 (s, 4H [13.2, 39.5]); ^{13}C δ 5.5 [9]; 76.0; 108.9; 128.5; 136.1; ^{119}Sn δ −288.03. Anal. Calcd for $C_{24}H_{22}Sn_2$: C, 52.62; H, 4.05; Sn, 43.33. Found: C, 52.08; H, 4.13; Sn, 42.37.

1,2-Bis(triprop-1-ynylstannylmethyl)benzene, 20: mp 122 °C; 61% yield; ^1H δ 2.2 (s, 18H [15]); 3.05 (s, 4H [96]); 7.3−7.5 (m, 4H); ^{13}C δ 5.5 [16]; 22.2 [570]; 75.0 [880]; 108.7 [178]; 125.7 [21]; 129.5 [20, 42]; 135.2; ^{119}Sn δ −266.4. Anal. Calcd for $C_{26}H_{26}Sn_2$: C, 54.23; H, 4.55; Sn, 41.22. Found: C, 53.31; H, 4.78; Sn, 42.05.

1,4-Bis(triprop-1-ynylstannylmethyl)benzene, 21: mp 109 °C; 62% yield; ^1H δ 1.85 (s, 18H [18]); 2.65 (s, 4H [14, 130]); 7.05 (s, 4H); ^{13}C δ 5.1 [20]; 27.3 [554]; 76.2 [849]; 106 [216]; 128.2 [26, 50]; 134.3 [32]; ^{119}Sn δ −263.6. Anal. Calcd for $C_{26}H_{26}Sn_2$: C, 54.23; H, 4.55; Sn, 41.22. Found: C, 53.74; H, 4.36; Sn, 41.95.

X-ray Crystallography. Crystal data collection and processing parameters are given in Table 1. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Nonius Kappa-CCD diffractometer equipped with an Oxford Cryosystems low-temperature device.[20] Data were collected at 150 K using Mo Kα radiation. The images were processed and equivalent reflections were merged; corrections for Lorentz−polarization and absorption were applied.[21] The structure was solved by direct methods,[22] and subsequent Fourier difference syntheses revealed the positions of all other non-hydrogen atoms. The asymmetric unit contains two halves of crystallographically independent molecules of $[Cl_3Sn(CH_2)_4SnCl_3]$, with each molecule lying across a crystallographic inversion center. After preliminary anisotropic refinements three Cl atoms gave elongated displacement ellipsoids. These atoms were subsequently “split”, modeled in terms of static 50:50 disorder [Cl(1) & Cl(11); Cl(2) & Cl(21); Cl(5) & Cl(51)], and refined in the anisotropic approximation. H atoms were placed in calculated positions and refined in a riding model. An extinction correction[23] and Chebychev weighting scheme[24] were applied in the final stages of refinement. All crystallographic calculations were performed using SIR92[22] and CRYSTALS.[25]

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Supporting Information Available: Tables with bond lengths, bond angles, atomic coordinates, and anisotropic displacement parameters for the structures of **8.** This information is available free of charge via the Internet at http://pubs.acs.org.

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[20] Cosier, J.; Glazer, A. M. *J. Appl. Crystallogr.* **1986**, *19*, 105.

[21] Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326.

[22] Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 1045−1050.

[23] Larson, A. C. *Crystallographic Computing*; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970; p 291.

[24] Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr.* **1979**, *A35*, 698.

[25] Watkin, D. J.; Prout, C. K.; Carruthers, R. J.; Betteridge, P. *CRYSTALS*; Chemical Crystallography Laboratory; University of Oxford, UK, 1996. Watkin, D. J.; Prout, C. K.; Pearce, L. J. *CAMERON*; Chemical Crystallography Laboratory; University of Oxford: UK, 1996.