Organotin Compounds. 31.[1] Dodecamethylcyclohexastannane and Dodecaperdeuteriomethylcyclohexastannane

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Pure dodecamethylcyclohexastannane (**1a**) and dodecaperdeuteriomethylcyclohexastannane (**1b**) have been prepared in high yields, whereas earlier attempts failed. Their ^{1}H NMR (for **1a**), ^{119}Sn NMR, IR, Raman, and mass spectra have been investigated and secure the identification. In solution, **1a** equilibrates even at 20 °C with three other cyclostannanes $(Me_2Sn)_n$, n being presumably 5, 7, and 8, more extensily at 80 °C. **1a** is the most stable of all. Thermal reactions of **1a** are described, including splitting off of free stannylenes Me_2Sn and formal insertion reactions of Me_2Sn units into C–Hal and Sn–Hal bonds.

Introduction

Peralkylated and perarylated cyclostannanes $(R_2Sn)_n$ have first been prepared and identified in the early sixties.[4-6] This was the end of old assumptions that σ-bonded stannylenes like Et_2Sn, Bu_2Sn, or Ph_2Sn might be stable compounds at room temperature.[6]

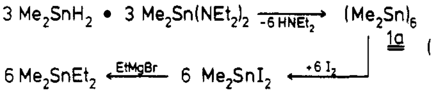
Uniform and mostly well-crystallized cyclostannanes $(R_2Sn)_n$ with four-, five-, six- (seven-), and nine-membered rings have been obtained; the ring size depends on both the kind of R and the method of preparation. So, $(Et_2Sn)_6$, e.g., forms nice yellow crystal needles, stable for months if light, oxygen, heat, and impurities are excluded. $(Et_2Sn)_9$, which is obtained with use of another method, behaves likewise.

But, many efforts to prepare a corresponding well-defined methyl derivative $(Me_2Sn)_n$ remained unsuccessful: yellow rubberlike polymers or waxes resulted, nonuniform, unstable, sparingly soluble, which were decomposed even by scattered daylight.[4,6] Another method[7] led to a product considered to be the hexamer, besides large amounts of polymers.

Our present interest in $(Me_2Sn)_n$ has its origin in our search for thermally generated free stannylenes Me_2Sn,[8] and we wish to report here the preparation of dodecamethylcyclohexastannane $[(CH_3)_2Sn]_6$ and its d_{12} derivative $[(CD_3)_2Sn]_6$, their identification by ^{1}H and ^{119}Sn NMR, Raman, IR, and mass spectroscopy, and several chemical reactions as well.

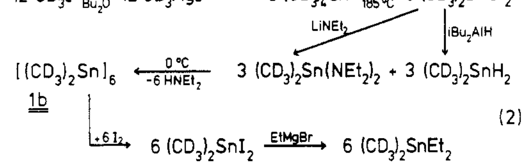
Results and Discussion

(A) Preparation of Dodecamethylcyclohexastannane (1a) and Dodecaperdeuteriomethylcyclohexastannane (1b). The condensation of equimolar amounts of Me_2SnH_2 and $Me_2Sn(NEt_2)_2$ under careful exclusion of air gave the same unsatisfying results as in earlier attempts.[4,6] But, careful reexamination of the experimental conditions finally led to **1a** as the only product in nearly quantitative yield, eq 1, when we excluded the bulk of daylight, lowered the temperature to at least 0 °C, and dried the precipitated cyclostannane carefully at 10^{-3} mm (20 °C). **1a** is a slightly yellow powder, sensitive toward oxygen and light, readily soluble in aromatics and other hydrocarbons, but insoluble in alcohols, as known from other compounds $(R_2Sn)_n$.[6] Many attempts to obtain acceptable crystals have failed so far. No redistribution reactions occur under these mild conditions, since degradation with iodine and successive treatment with EtMgBr leads exclusively to Me_2SnEt_2: see eq 1. In concentrated benzene solution, ^{1}H NMR exhibits only one CH_3 signal, at 0.63 ppm, and ^{119}Sn NMR also exhibits only one peak, at −231.04 ppm: see (C). Thus, the substance is a uniform compound within the range of NMR accuracy. Mass spectroscopy shows the molecular ion $Me_{12}Sn_6^+$ as the heaviest particle, and, moreover, all the fragments to be expected for **1a**. All IR and Raman peaks are in accordance with the calculated ones: see (C). We are dealing, therefore, with the hexamer **1a**.



(1)

The corresponding dodecaperdeuteriomethylcyclohexastannane (**1b**) could be obtained in pure form and identified in a similar way: see eq 2. Besides **1b**, the dihydride and the amide are new substances, whereas $(CD_3)_4Sn$[9] and the dichloride[10] have been described previously. **1b** exhibits no ^{1}H NMR signal, and all other facts including IR and Raman spectroscopy are in agreement with the given formula.



(2)

(B) Equilibration of 1a in Solution. When the concentrated solution of **1a** in benzene is diluted, in both the ^{1}H and the ^{119}Sn NMR a new, sharp singlet appears at 0.53 or −241.40 ppm, respectively, besides that of **1a**, and disappears upon reconcentration. Heating of a solution containing **1a** and the new species in a 1:1 ratio at room temperature up to 80 °C yields reversibly a 1:4 ratio within

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Table I. Observed and Calculated[a] IR and Raman Frequencies (cm^{-1}) of the Cyclohexastannanes $[(CH_3)_2Sn]_6$ (1a) and $[(CD_3)_2Sn]_6$ (1b)

assignt (X = H or D)	$[(CH_3)_2Sn]_6$ (**1a**) IR (293 K) obsd[b,c]	calcd	IR (40 K), obsd[d]	Ra (293 K) obsd	calcd	Ra (40 K) obsd	$[(CD_3)_2Sn]_6$ (**1b**) IR (293 K) obsd[b]	calcd	Ra (293 K) obsd	calcd	Ra (40 K) obsd
ν_{as}(C–X)	2970 m, br			2985 w, br		2990 w, br	2233 w		2240 m, br		2245 m, br
ν_s(C–X)	2903 m, br			2916 w, br		2920 w, br	2112 m		2118 s, br		2122 m, br
δ_{as}(XCX)	1454 w, br			1410 w, br		1405 w, br	1020 m, br		1026 w, br		1023 w
	1375 w, br										
δ_s(XCX)	1190 m			1185 s		1190 m	926 m		919 sh, m		912 m
	1183 m			1179 m		1177 s			907 m		902 s
ρ(CX_3)	767 s		766 s	785 w, br		785 w, br	594 s		607 m		600 w
			715 s, sh				543 s				
	708 s, br		699 s								
ν(Sn–C)	508 s	509	508 s	510 s	509	511 s	463 s	472	468 s	472	469 s
	496 s	494	496 s				449 s	455			
		493						454			
2 × ν(Sn–Sn)				418 m		430 w			412 m		423 w
ν(Sn–Sn) + δ(Sn–SnC)				250 w					239 m		
ν(Sn–Sn)	215 m	197		210 s	221	214 s			205 s	220	210 s
ν(Sn–Sn)[e]				173 s	178	187 m			163 vs	175	169 s
δ(CSnC)	135 m, br	141		146 vs	141	156 vs			135 s	130	148 s
		139				133 m, sh			115 s	116	118 m
δ(SnSnC)	80 w, sh	89		82 w	78	89 w, br			70 m	73	73 w, br
	72 m	85									

[a] Skeletal vibrations, symmetry D_{3d}. [b] KBr pellet, 4000 – 400 cm^{-1}. [c] PE pellet, 600 – 200 cm^{-1}; FIR 250 – 50 cm^{-1} suspended in Nujol. [d] KBr pellet, recorded region: 900 – 400 cm^{-1}. [e] Breathing mode of the six-membered ring.

less than 1 h. We are faced with the surprising fact that the cyclostannane **1a** equilibrates with another cyclostannane, $(Me_2Sn)_n$ (a Me_2Sn polymer containing also MeSn and/or Me_3Sn groups can be excluded from the degradation with iodine; see eq 1), spontaneously and reversibly even at room temperature.

Besides the two main signals mentioned two other, very weak singlets can be seen in the ^{119}Sn NMR at −243.40 and −244.94 ppm (see Figure 1) also within the region of cyclostannanes. (In the ^1H NMR, no corresponding signals are detected.) All three new ^{119}Sn signals become stronger at 80 °C to the expense of that at −231.04 ppm. Since MeSn and Me_3Sn groups are to be excluded and since all four signals are close together, $(Me_2Sn)_n$ (n = 3, 4) is not to be discussed for these compounds, because the corresponding signals should be expected in more remote positions.[11] Further ^{119}Sn NMR data of comparable compounds, unfortunately, are not available at present.

In this state of our investigations, we ascribe, therefore, the signal at −241.40 ppm (and the corresponding signal at 0.53 ppm in the ^1H NMR) to the cyclostannane with n = 5, **2a**, and the two others tentatively to n = 7 and 8. A detailed study will be carried out later. What mainly happens it seems is eq 3 the hexamer **1a** being more stable

$$140\ \underset{\mathbf{1a}}{(Me_2Sn)_6} \rightleftharpoons 168\ \underset{\mathbf{2a}}{(Me_2Sn)_5} \rightleftharpoons 120\ (Me_2Sn)_7 \rightleftharpoons 105\ (Me_2Sn)_8 \qquad (3)$$

than the other oligomers. The presence of higher oligomers is demostrated by rapid evaporation of an equilibrium mixture (eq 3) at 12 mm until a very viscous rubberlike product results. Its mass spectrometry gives, besides **1a**, $Me_{14}Sn_7^+$ as the heaviest ion and all the fragments thereof to be expected.

A similar equilibration may occur also to other cyclostannanes, $(R_2Sn)_n$, formerly[4-6] thought to be stable even at higher temperatures. Thus, a sample of pure, cystalline $(Bu_2Sn)_6$ gives, during mass chromatography,[12] a mixture of $(Bu_2Sn)_5$, $(Bu_2Sn)_6$, $(Bu_2Sn)_7$, and other oligomers.[13]

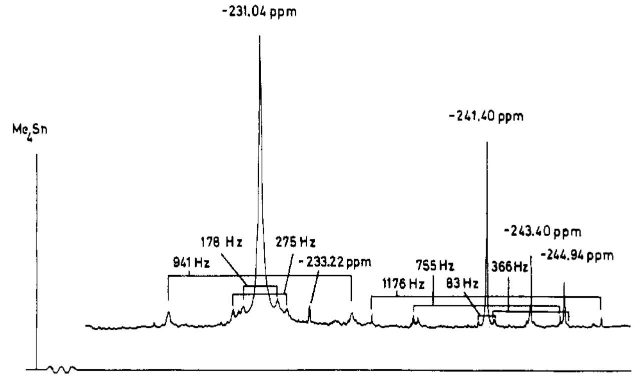


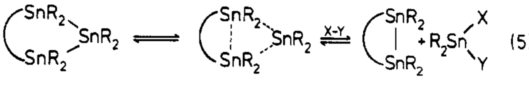
Figure 1. ^{119}Sn NMR spectrum of an equilibrated mixture of $(Me_2Sn)_n$ following eq 3 in toluene/C_6D_6 (1:1) at 25 °C (c = 1 M Me_2Sn). For **1a** (−231.04 ppm) and **2a** (−241.40 ppm), $^1J_{SnSn}$ and $^2J_{SnSn}$ are given: for **1a** also $^3J_{SnSn}$ measured values of $J(^{119}Sn-^{117}Sn)$. The coupling of 83 Hz probably is a ^{13}C coupling. Traces of nonidentified impurity cause the very weak peak at −233.22 ppm.

It has to be discussed, whether the equilibrations described here proceed via free stannylenes R_2Sn. In fact, at 80 °C an equilibrium following eq 4 has been found[14]

$$(Me_2Sn)_n + n\ Me_2SnX_2 \rightleftharpoons n\ Me_2Sn(X)\text{-}Sn(X)Me_2 \qquad (4)$$

X=SPh, Br

with a formal insertion product of a stannylene. But, this is by no means a proof of the existence of free stannylenes. On the contrary, a stannylenoid mechanism (eq 5) may be


(5)

operative here passing transition states as indicated.

(C) Spectroscopy of 1a and 1b. Figure 1 gives the ^{119}Sn NMR data for the $(Me_2Sn)_n$ compounds mentioned so far. The compound with n > 6 has to be excluded for **1a** following the discussion given in (A) and (B), including

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[11] Compare, e.g., the corresponding ^{29}Si NMR data for $(Et_2Si)_n$: −16.04 for n = 4, −30.36 for n = 5, −30.49 for n = 6, −30.03 for n = 7, and −27.70 for n = 8. Carlson, C. W.; West, R. *Organometallics* **1983**, *2*, 1792.

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the results of mass spectroscopy and that below.

Details of the mass spectrometry are described in the Experimental Section.

As a further proof for the structures of **1a** and **1b** IR and Raman investigations of the pure compounds have been carried out at room temperature and at 40 K. This seemed to us of a more general importance, since only restricted knowledge with this respect could be found in the literature concerning oligo- and polystannanes.[7,15,16] Table I gives the results. All bands above 540 cm^{-1} are assigned to vibrations of the CH_3 groups and are not discussed here in detail since they are without value for the present considerations.

For the identification of a cyclostannane or a mixture thereof, assignment of the skeletal vibrations is necessary. In order to check this, a normal coordinate analysis[17] for **1a** has been carried out assuming a chair conformation of the six-membered ring with tetrahedral Sn surroundings and replacing the CH_3 groups by mass points of the mass 15. The same has been done for the perdeuterio derivative **1b**, but with replacement of CD_3 by points of a mass of 18.

As can be seen from Table I, there is a fair agreement between the measured values and those calculated for **1a** and **1b**. Especially elusive is the very intense Raman ring breathing mode at 173 cm^{-1} for **1a**, not visible in the IR spectrum as to be postulated, which shifts down to 163 cm^{-1} for the deuterated **1b**, as expected, and becomes even more intense and sharper. This and the loss of 70% of the intensity by going down to 40 K for both **1a** and **1b** (see Table I) is an additional argument for the assignment being correct. The antisymmetric Sn–Sn stretching modes are observed at 215 (IR) and 210 cm^{-1} (Ra) for **1a** and at 205 cm^{-1} and at 205 cm^{-1} (Ra) for **1b**. During cooling down, below about 77 K a thermochromism is observed, both **1a** and **1b** becoming colorless without any change of the spectra and yellow again when the temperature is raised.

Other Sn–Sn stretching or ring breathing modes than those mentioned cannot be detected. This means that the two compounds **1a** and **1b** both are, within the limit of accuracy (≥95%), uniform cyclohexastannanes.

(D) Some Reactions of 1a. $(Me_2Sn)_n$ has been used for photochemical insertions of Me_2Sn units into C–Hal, O–O, Sn–H, and Sn–C bonds and for additions to π systems like 2,3-dimethylbutadiene and a number of aldehydes and ketones.[3,19,20] But, no decision between free stannylene and stannylenoid mechanisms could be made at that time.

The knowledge on thermal reactions of **1a** is still very restricted. Besides the insertion of Me_2Sn units into Sn–X bonds (X = Br, SPh)[14] mentioned above an insertion into the C–Br bond of BuBr (eq 6) has been observed (besides

$$\tfrac{1}{6}\ \underline{\underline{1a}} + \text{BuBr} \xrightarrow[\text{neat, 10 h}]{80\ ^\circ\text{C}} \underset{10\ \%}{\text{Bu-Me}_2\text{Sn-Br}} \qquad (6)$$

a mixture of other products) and also into the C–I bond of MeI.[21] Reactions with (*E,E*)-1,4-diphenylbutadiene, muconic acid dimethyl ester, and a 1,1,6,6-tetrasubstituted diallene,[22] which did react stereospecifically with a free germylene, Me_2Ge,[23] could not be effected thermally. A mixture of **1a** and the pentamer **2a** reacts with tetracyanoethylene (TCNE) spontaneously in benzene at 20 °C, presumably via single electron transfer, giving a dark green solution (ESR, TCNE anion radical), which deposits a greenish solid. Its average composition is $TCNE{\cdot}2.6Me_2Sn$, and it shows Sn—N=C ketenimine peaks (IR) at 2134 cm^{-1} (s) and peaks of $Sn{-}C(CN)_2$ groups at 2200 cm^{-1} (m) as well.[24] $(Et_2Sn)_n$ behaves similarly, giving a brown product of analogous kind.[24] **1a** did not react with organotin chlorides, neither neat nor in THF. Surprisingly, admixing of LiCl to the THF solution at room temperature catalyzed a smooth reaction with quantitative consumption of **1a** and generation of the (unsymmetric) distannane (eq 7).[25] Besides, some trialkyltin monochloride was found,

$$\tfrac{1}{6}\ \underline{\underline{1a}} + R_2SnCl_2 \xrightarrow[\text{THF, LiCl, 2–4 h}]{20\ ^\circ\text{C}} R_2\underset{\substack{|\\ Cl}}{Sn}{-}\underset{\substack{|\\ Cl}}{Sn}Me_2 \qquad (7)$$

R = Me: yield 75%
Et: " 60%

apparently resulting from a consecutive degradation of the labile distannane. With one of the R groups being Ph or *t*-Bu the reaction (eq 7) was very slow at 20 °C and the yield low. At −20 °C the educt mixture is stable in the presence of LiCl in THF. **1a** is not affected by LiCl but R_2SnCl_2 is. Its ^{119}Sn NMR signal is shifted (at −75 °C in THF) from −100.4 to −167.8 ppm; its ^1H NMR Me–Sn coupling (THF) at room temperature increases from 82 to 92 Hz. The kind of LiCl catalysis, however, still requires further investigation.

In all these reactions both the mechanism and the occurrence of intermediate free stannylenes Me_2Sn remain open.

It seemed important, therefore, to investigate whether free stannylenes Me_2Sn can be generated thermally from **1a**, especially since we had observed the rapid equilbration in solution (eq 3). Cyclostannanes with higher residues, e.g., $(Et_2Sn)_6$, $(Bu_2Sn)_6$, and $(Ph_2Sn)_6$, behaved rather stable upon heating without solvent, even during mass spectrometry. In all these cases, the molecular ions $(R_2Sn)_6^+$ could be observed and all the fragment ions following from a stepwise degradation as well.[12] As mentioned above, the same was the case with **1a** when analyzed at 180–200 °C. But, when we heated it slowly within the probe of the mass spectrometer at about 50 °C, at first only monotin particles were registered and fragments containing more than one tin atom only above 120 °C.

This encouraged us to try a matrix isolation of whatever came out of **1a** at 6×10^{-6} mm. The thermolysates were isolated in Argon matrices at 5 K. When heating **1a** at 120 °C, well-resolved IR spectra of good intensity could be recorded showing exclusively the bands to be expected and calculated for Me_2Sn.[8] The absence of Sn–Sn vibrations (see Table I) was confirmed by Raman matrix spectroscopy. Clearly the free stannylene Me_2Sn has been obtained by thermal splitting of **1a** and likewise the free stannylene $(CD_3)_2Sn$ from **1b**.[8]

Experimental Section

General Comments. All reactions have been carried out under argon, as most of the organotin compounds used are sensitive toward oxygen and/or moisture. The solvents were dried according to standard methods and distilled under argon. $Me_2Sn(NEt_2)_2$ and Me_2SnH_2 were prepared from Me_2SnCl_2 by established methods[26,27] ^1H NMR, Varian EM 360 A, 60 MHz,

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chemical shifts in δ against Me_4Si as internal reference; ^{119}Sn NMR, Bruker AM, 300 MHz, chemical shifts in δ against Me_4Sn as internal reference; IR, Perkin-Elmer 325, 457, 577; Raman, Coderg T 800; Laser, Spectraphysics, 514.5 nm Ar^+, 641.1 nm Kr^+; mass spectra, Varian CH 5; GC, Varian 1800 40/3 and 1700 40/1, Perkin-Elmer F 20 H; elemental analysis, Heraeus Mikro CHN Monar and elemental analyzer, Carlo Erba MOD 1106.

Dodecamethylcyclohexastannane, $(Me_2Sn)_6$ (1a). Me_2SnH_2 (3.3 g, 21.8 mmol) was added dropwise in the dark (by wrapping the flask with aluminium foil) to well-stirred $Me_2Sn(NEt_2)_2$ (6.4 g, 21.8 mmol) at 0 °C (measured in the mixture). Stirring of the resulting yellow solution was continued at 20 °C for 30 min. After the solution was diluted with $HNEt_2$ (5 mL), the cyclostannane was precipitated by adding slowly MeOH (20 mL) to the vigorously stirred solution. Decantation of the solvents and thorough drying of the residue at 10^{-3} mm (20 °C) for 15 h afforded **1a** as an amorphous, yellow, light- and air-sensitive powder: yield 6.0 g (92.3%).

The cyclostannane, dissolved in benzene (equilibrium mixture **1a** + **2a**), was degradated by I_2 in benzene solution to Me_2SnI_2 [^1H NMR (benzene) δ 0.90 (s, $^2J_{HSn}$ = 60/64 Hz, 6 H)] leading to a complete decolorization of the solution.[4] A 0.09093-g sample of **1a** required 0.15178 g of I_2 (98%; calcd 1 mol of I_2/equiv of Me_2Sn). Alkylation with $EtMgBr/Bu_2O$ yielded only Me_2SnEt_2 (GC, 4 m DC 200; Me_3SnEt, $MeSnEt_3$ > 0.1%). For ^1H and ^{119}Sn NMR see Figure 1; for IR and Raman data see Table I. MS (70 eV, 180–200 °C): *m/e* (relative intensity) 891 (M^+, 0.4), 876 ($M - Me^+$, 0.3), 759 ($Me_{11}Sn_5^+$, 0.4), 744 ($Me_{10}Sn_5^+$, 0.4), 729 ($Me_9Sn_5^+$, 0.5), 611 ($Me_9Sn_4^+$, 1), 596 ($Me_8Sn_4^+$, 0.7), 581 ($Me_7Sn_4^+$, 0.7), 551 ($Me_5Sn_4^+$, 0.6), 521 ($Me_3Sn_4^+$, 0.3), 491 ($MeSn_4^+$, 0.3), 476 ($Me_8Sn_3^+$, 0.4), 461 ($Me_7Sn_3^+$, 2), 446 ($Me_6Sn_3^+$, 0.8), 431 ($Me_5Sn_3^+$, 0.9), 416 ($Me_4Sn_3^+$, 0.5), 401 ($Me_3Sn_3^+$, 0.7), 386 ($Me_2Sn_3^+$, 0.4), 371 (Sn_3^+, 0.4), 328 ($Me_6Sn_2^+$, 4), 313 ($Me_5Sn_2^+$, 3), 283 ($Me_3Sn_2^+$, 2), 253 ($MeSn_2^+$, 2), 253 ($MeSn_2^+$, 2), 238 (Sn_2^+), 1), 180 (Me_4Sn^+, 1), 165 (Me_3Sn^+, 100), 150 (Me_2Sn^+, 33), 135 ($MeSn^+$, 40), 120 (Sn^+, 21).

The assignment of the peaks in the MS spectra mentioned was done by means of the isotope patterns as given by the computer program ISOTOP.[12]

$(CD_3)_4Sn$ was prepared from CD_3I (50 g, 0.345 mol), magnesium turnings (11.1 g, 0.457 mol), and $SnCl_4$ (17.5 g, 7.5 mL, 0.067 mol) according to Me_4Sn:[28] yield 9.8 g (77%); bp 70 °C.

$(CD_3)_2SnCl_2$. $SnCl_4$ (12.8 g, 5.5 mL, 0.049 mol) was added dropwise under vigorous stirring to $(CD_3)_4Sn$ (9.4 g, 0.049 mol) at 0 °C. After additional stirring at 20 °C for 1 h, the reaction mixture was slowly heated to 185 °C and kept there for 1 h. On cooling colorless crystals of $(CD_3)_2SnCl_2$ appeared and were recrystallized from toluene: yield 16.4 g (74%); mp 109 °C.

$(CD_3)_2Sn(NEt_2)_2$. $HNEt_2$ (6.50 g, 9.2 mL, 0.089 mol) was added dropwise at 0 °C to a solution of *n*-BuLi (93.7 mL, 0.79 M), and the reaction mixture warmed to 60 °C for 2 h, followed by additional stirring at 20 °C for 12 h. A solution of $(CD_3)_2SnCl_2$ (8.35 g, 0.037 mol) in diethyl ether (90 mL) was added and the mixture heated at 60 °C for 3 h. After centrifuging in order to separate LiCl and removing the solvents from the yellow solution, the residue (10 mL) was distilled in vacuo through a 10 cm-Vigreux column: yield 8.1 g (73%); bp 54–55 °C (0.15 mm; ^1H NMR (neat) δ 1.00 (t, 6 H, NCH_2CH_3), 2.97 (q, $^3J_{HSn}$ = 43/45 Hz, 4 H, NCH_2CH_3).

$(CD_3)_2SnH_2$. To a well-stirred cooled (−5 °C) solution of *i*-Bu_2AlH (9.7 g, 12.4 mL, 0.068 mol) in dihexyl ether (15 mL) was added $(CD_3)_2SnCl_2$ (7.7 g, 0.034 mol) in such portions that the temperature did not rise above 0 °C. After the addition was complete, the stirred solution warmed up to 20 °C. The formed $(CD_3)_2SnH_2$ was distilled from the reaction mixture (20 °C (10^{-2} mm)), the receiver being cooled with liquid N_2. Purification was accomplished by an additional distillation (0 °C (12 mm)), using a cooled (−70 °C) Schlenk flask as receiver: yield 2.5 g (47%); ^1H NMR (neat) δ 4.30 (s, $^1H_{HSn}$ = 1712/1717 Hz, 2 H, SnH).

$[(CD_3)_2Sn]_6$ (1b). **1b** was prepared from $(CD_3)_2Sn(NEt_2)_2$ (1.14 g, 3.8 mmol) and $(CD_3)_2SnH_2$ (0.59 g, 3.8 mmol) in a manner identical with that described for **1a**: yield 0.9 g (78%). **1b** was identified by its IR and Raman spectra (see Table I) and a degradation with I_2. Treating **1b**, dissolved in benzene, with a diluted benzene solution of I_2 followed by an alkylation of the reaction mixture with $EtMgBr/Bu_2O$ gave exclusively $(CD_3)_2SnEt_2$ (GC, 2 m SE 30 and 0.5 m OV 101; $(CD_3)_3SnEt$, CD_3SnEt_3 < 0.1%). A 0.08015-g sample of **1b** required 0.13265 g of I_2 (97%: calcd 1 mol of I_2/equiv of $(CD_3)_2Sn$). There is no ^1H NMR signal (benzene). For IR and Raman data see Table I.

$Me_2ClSn-SnClMe_2$.[25] Me_2SnCl_2 (1.32 g, 6.0 mmol) and **1a** (1.94 g of a 46% solution in toluene, 6.0 molar equiv of Me_2Sn) were resolved in THF (10 mL) (^1H NMR no reaction). After the addition of dry LiCl (1.0 g) and stirring, a slightly exothermal reaction was observed (maximum 30 °C) and finished after 2 h: yield in the mixture, 75% of the desired product, besides 17% of Me_3SnCl (^1H NMR). After evaporation at 20 °C (10^{-3} mm) the residue was twice resolved in CH_2Cl_2 (5 mL) and again evaporated in order to remove the THF. Then CH_2Cl_2 (30 mL) was added and the mixture, after filtration, cooled down to −30 °C: the colorless product crystallizes: yield 1.55 g (70%); decomposition at about 80 °C; ^1H NMR ($CDCl_3$) δ 0.93 (s, $^2J_{HSn}$ = 53.5 Hz, $^3J_{HSn}$ = 13.0 Hz, 12 H, $ClSnMe_2$).

$Et_2ClSn-SnClMe_2$[25] was obtained in analogous way (maximum 30 °C): yield 60%, ^1H NMR (CH_2Cl_2) δ 0.90 (s, $^3J_{HSn}$ = 12.5 Hz, 6 H, $ClSnMe_2$), 1.20–1.87 (m, $^2J_{HSn}$ = 52.5 Hz, 10 H, $ClSnEt_2$); ^{119}Sn NMR (THF, −80 °C) δ −136.5, −148.3.

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Registry No. **1a**, 63923-84-2; **1b**, 85363-44-6; **2a**, 98088-27-8; Me_2SnI_2, 2767-49-9; Me_2SnEt_2, 4282-05-7; $(CD_3)_2SnH_2$, 85363-43-5; $(CD_3)_2SnCl_2$, 80048-65-3; $(CD_3)_2Sn(NEt_2)_2$, 85363-42-4; $(CD_3)_2SnI_2$, 98088-24-5; $(CD_3)_2SnEt_2$, 98088-25-6; $Me_2ClSn-SnClMe_2$, 58529-40-1; $(CD_3)_4Sn$, 29289-11-0; $Et_2ClSn-SnClMe_2$, 98088-26-7; Et_2SnCl_2, 866-55-7; Me_2SnH_2, 2067-76-7; $Me_2Sn(NEt_2)_2$, 1185-22-4; Me_2SnCl_2, 753-73-1.

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