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Vinylstannanes: synthesis and characterization

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Abstract

Primary, secondary and tertiary vinylstannanes **2a–2f** are synthesized by reduction of the corresponding chloro(vinyl)stannanes. They are characterized by their spectral data (IR, NMR (^{119}Sn, ^{13}C, ^{1}H) spectroscopy and mass spectrometry). The ^{119}Sn chemical shifts and $^{1}J_{SnH}$ and $^{1}J_{SnC}$ of vinylstannanes are compared with the data reported for the corresponding alkyl- and aryl-stannanes. Compounds **2** decompose slowly at room temperature in benzene ($\tau_{1/2}$ 1–3 days). The formation of divinylchlorostannane and the use of trivinylstannane as a reducing agent are also reported.

Keywords: Vinylstannanes; Tin; Hydride; Reduction; NMR-study

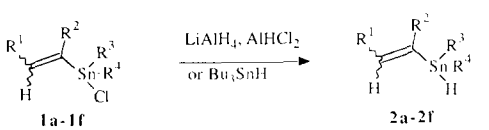
1. Introduction

Although α-unsaturated silanes [1] and germanes [2] have been well known compounds for a long time, only a few of the corresponding tin hydrides have been described. In 1959, Brinkmann and Stone [3] reported the synthesis and the characterization by IR spectroscopy of the ethenylstannane. It was prepared by addition of lithium aluminum hydride (LAH) on the trichloro(ethenyl)stannane and obtained in a low yield after a difficult purification. To our knowledge, only two other derivatives have been characterized. Dimethyl(trifluorovinyl)stannane [4] was prepared by reaction of dimethylstannane with the dimethylbis(trifluorovinyl)stannane, and a borovinyldialkylstannane [5] was observed by NMR spectroscopy among the reaction products arising from chlorostannane with trimethylstannane. The low stability of these compounds, due to the presence on the same tin atom of a hydrogen and of an unsaturated substituent, can explain their rarity. However, it is of interest to synthesize these species, to define their spectroscopic characteristics, and their stability. The present paper describes a general preparation of primary, secondary and tertiary low-boiling vinylstannanes and their spectral characterization. We also describe the synthesis of the divinylchlorostannane and the chemoselective reduction of a dibromoalkane by the trivinylstannane.

2. Results and discussion

2.1. Preparation

The chloro(vinyl)stannanes **1a–1f** have been prepared as previously reported by reaction of a tetravinyl- [6] or a vinyltributyl-stannane [7] with a polychlorostannane. To perform the reduction of **1a–1f** to the corresponding volatile primary, secondary, or tertiary vinylstannane **2a–2f**, LAH, dichloroalane [8], or tributylstannane [9] were used as reducing agents



1a–1f **2a–2f**

1a : R^1, R^2 = H; R^3, R^4 = Cl
1b : R^1, R^2 = H; R^3 = H_2C=CH, R^4 = Cl
1c : R^1, R^2 = H; R^3, R^4 = H_2C=CH
1d : R^1, R^2 = H; R^3, R^4 = CH_3
1e : R^1 = H; R^2 = CH_3; R^3, R^4 = Cl
1f : R^1 = CH_3; R^2 = H; R^3, R^4 = Cl

2a : R^1, R^2, R^3, R^4 = H
2b : R^1, R^2, R^4 = H; R^3 = H_2C=CH
2c : R^1, R^2 = H; R^3, R^4 = H_2C=CH
2d : R^1, R^2 = H; R^3, R^4 = CH_3
2e : R^1, R^3, R^4 = H; R^2 = CH_3
2f : R^1 = CH_3; R^2, R^3, R^4 = H

Scheme 1.

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Table 1
Selected data of vinylstannanes **2a–2g**

Compounds	Yield [a] (%)	$\tau_{1/2}$ [b] (h)	NMR [c]				IR [d]		
			δ_{1H} (SnH) (ppm)	δ_{119Sn} (ppm)	$^1J_{SnH}$ (Hz)	$^1J_{SnC}$ (Hz)	$\nu_{=CH}$ (cm^{-1})	ν_{Sn-H} (cm^{-1})	$\nu_{C=C}$ (cm^{-1})
2a	60	20	4.64	−360.7	1917.3	531.9	3042	1865	[e]
2b	67	24	5.36	−263.3	1918.3	519.2	3039	1855	[f]
2c	74	48	5.89	−199.4	1948.0	516.4	3040	1855	[f]
2d	75	72	4.85	−133.7	1798.5	477.0	3039	1830	[f]
2e	66	24	4.76	−346.9	1882.0	477.0	3050	1865	1620
2f ($Z+E$)	64	24	4.48 (Z)	−418.9 (Z)	1896.0 (Z)	515.3	3062	1840	1600
			4.65 (E)	−362.3 (E)	1896.2 (E)				
2g	65		7.24	−88.9	2501.0	603.0	–	–	–

[a] Determined by ^1H NMR.
[b] Determined by ^1H NMR from a 2% concentration of **2** in C_6D_6.
[c] in C_6D_6.
[d] In gaseous phase; the pressure of **2** is of about 100 mbar.
[e] Not observed [3].
[f] Not observed.

(Scheme 1). To limit decomposition, compounds **2a–2f** were distilled in vacuo from the cooled reaction mixture (0°C) during the course of the addition and separated from the solvent by a cold trap (−60°C) before condensation (−196°C) [10]. Stannanes **2a–2f** were obtained pure in ca. 60% yield. Whichever the chlorostannane and the reducing agent, we never observed the reduction of the carbon–carbon double bond. This efficient procedure is, however, limited to volatile compounds.

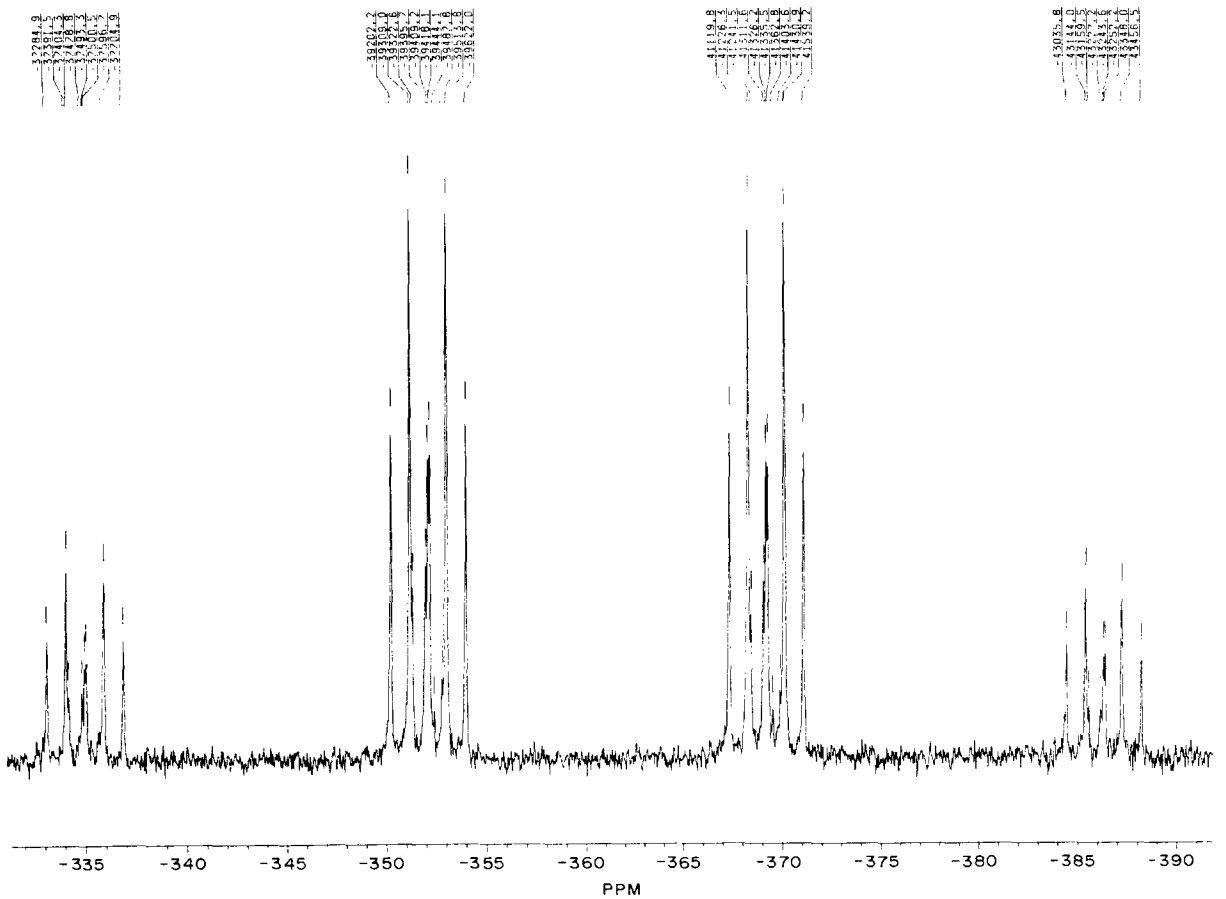


Fig. 1. ^{119}Sn NMR spectrum (gate decoupling) of ethenylstannane **2a**.

2.2. Spectral characterization

Compounds **2a–2f** were characterized by gas-phase IR and NMR (^{1}H, ^{119}Sn and ^{13}C) spectroscopy (Table 1). The $\nu_{C=C-H}$ ranged from 3039 (**2b**) to 3062 cm^{-1} (**2f**) and the ν_{Sn-H} observed near 1860 cm^{-1} are characteristic of such compounds [3]. The presence of the stannanes **2** is also confirmed by the observation of the corresponding $[M-H]^+$ ion by high resolution mass spectrometry (HRMS).

The ^{1}H and ^{13}C NMR data allow an unambiguous structural assignment since the chemical shifts and the coupling constants are typical of vinyltin derivatives [11]. The more characteristic NMR data of vinylstannanes **2a–2f** are the ^{119}Sn chemical shifts, and $^1J_{SnH}$ and $^1J_{Sn-C}$ (Fig. 1).

The ^{119}Sn chemical shifts of vinylstannanes **2a–2f** depend on the number and on the nature of the substituents on the tin atom and the resonances of primary vinylstannanes are at higher field than those of the secondary and tertiary derivatives (Table 1). A vinyl substituent leads to a chemical shift to higher field than that observed for the corresponding alkyl or aryl derivative [12]. Thus, the ^{119}Sn chemical shifts of ethenylstannane **2a**, ethylstannane and phenylstannane are at δ_{119Sn} −360.7, −282 [12], and −320 ppm [12], respectively. Similar high-field displacements are also observed for the chemical shift of di- (δ_{119Sn} (**2b**) −263.3 ppm) and tri- substituted vinylstannanes (δ_{119Sn} (**2c**) −199.4 ppm) compared to the chemical shifts of the corresponding alkyl- (δ^{119}Sn (Et_2SnH_2) −231 ppm [12]; δ^{119}Sn (Et_3SnH) −67 ppm) [13] or aryl derivatives (δ^{119}Sn (Ph_2SnH_2) −234 ppm; δ^{119}Sn (Ph_3SnH) −148 ppm) [12].

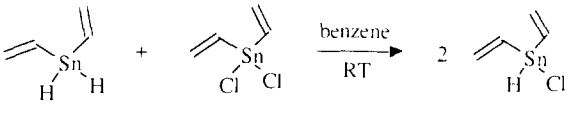
The $^1J_{SnH}$ values are higher than those usually observed for alkylstannanes and similar to those of aryl derivatives. Values of 1917.3 Hz and of 1948.0 Hz were observed for **2a** and **2c**, respectively. The corresponding coupling constants of ethyl- triethyl-, phenyl- and triphenyl-stannane are of 1790.1, 1611.3, 1921.5 and 1935.8 Hz, respectively [14] (SnH_4, which can be considered as a reference has a $^1J_{SnH}$ of 1932.6 Hz). It is generally accepted [15] that the Fermi-contact interaction constitutes a dominant factor in the spin-spin coupling mechanism. The vinyl substituents on the tin atom of **2a–2f** induce more s character in the Sn–H orbitals, which enhances the Fermi-contact interaction and generates higher values of $^1J_{SnH}$. Electronegative substituents are believed to cause a rehybridization at the element to which they are attached [16]. This is demonstrated by the higher $^1J_{SnH}$ occurring on substitution of a hydrogen by a chlorine atom ($\delta_{Sn}(Et_2SnH_2)$ 1691.1 Hz [14]: $\delta_{Sn}(Et_2SnH_2)$ 2007.8 Hz). This also explains the $^1J_{SnC}$ values of **2a–2f** which range between those of vinylalkylstannanes and vinylchlorostannanes. As an example, $^1J_{SnC}$ between tin and the sp^2 carbon atom of vinylstannane **2a** is 531.9 Hz; values of 1027.0 Hz and 375.5 Hz are observed for the corresponding coupling constant of ethenyltrichlorostannane **1a** and ethenyltributylstannane, respectively. In such cases, the electronegative chlorine atoms lead to an increase of the s character of the Sn–C (**1a**) and the butyl substituents lead to the converse [16].

Similar observations of chemical shifts and ^1J coupling constants have already been reported for other vinylic heterocompounds and particularly for silicon derivatives [17]. Thus, in the ^{29}Si NMR spectra, the resonance of ethenylsilane **3a** (δSi −64.0 ppm; $^1J_{SiH}$ = 199.4 Hz) is observed at higher field than that of ethylsilane **3b** (δSi −56.4 ppm; $^1J_{SiH}$ = 191.6 Hz) or phenylsilane **3c** (δSi −60.9 ppm; $^1J_{SiH}$ = 199.3 Hz) [17] and the $^1J_{SiH}$ coupling constants are in the sequence: $^1J_{SiH}$ (**3b**) < $^1J_{SiH}$ (**3c**) ≈ $^1J_{SiH}$ (**3a**).

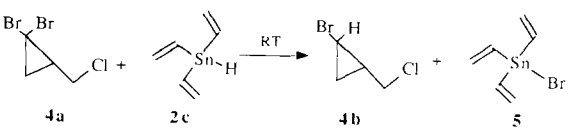
2.3. Stability and chemical properties

Vinylstannanes **2** decompose slowly at room temperature in benzene. The half-life of **2a–2g** depends on the substituents on the tin and increases from primary (**2a**, **2e**, **2f**) to tertiary derivatives (**2c**) or with the presence of alkyl groups (**2d**). Some phenyl derivatives such as diphenylstannane has low stability at room temperature [18].

The vinyl substituents on the tin atom of stannanes **2a–2f** does not significantly modify the chemical properties of vinylstannanes in comparison with alkyl or aryl derivatives [19]. Thus, the reaction of divinylstannane **2b** at room temperature with an equimolar amount of divinyldichlorostannane **1b** in octadeuterotoluene leads to the chloro(divinyl)stannane **2g** which has been characterized by ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy (Eq. (1), Table 1). Similar reactions have been widely used to prepare dialkylchlorostannanes starting from the corresponding dialkylstannanes [20].



Like alkyl- and aryl-stannanes, vinylstannanes **2** are reducing agents. As an example, the reduction of dibromocyclopropane **4a** by trivinylstannane **2c** to the corresponding bromocyclopropane **4b** has been performed at room temperature (Eq. (2) [21]. In these conditions, compound **2c** is stable enough to act as a reagent.



In summary, a preparative method has been developed for the synthesis of volatile primary, secondary, and tertiary vinylstannanes, in good yield. Extension to the preparation of other unstabilized tin derivatives is currently in progress.

3. Experimental section

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300P spectrometer; ^{29}Si and ^{119}Sn NMR spectra were recorded on a Bruker AC 300C spectrometer. Chemical shifts are in ppm relative to internal $SiMe_4$ for ^{1}H and ^{13}C spectra and external Me_4Sn for ^{119}Sn spectra IR spectra of vinylstannanes were obtained on a Perkin-Elmer 1420G instrument. High-resolution mass spectra mass analysis of a kinetic energy (MIKE) and collision activated dissociation analysis of ion kinetic energy (CAD-MIKE) were recorded on a Varian MAT 311 spectrometer. Special equipment was used for recording the IR spectrum of **2a–2f** in the gas phase: a small pyrex tube (l = 10 cm; i.d. = 3 cm) equipped with a stopcock and sealed at each end with a KBr window was filled with pure vinylstannane to a pressure of 100 mbar. To record the mass spectrum, compound **2** was introduced directly from a cell into the ionization chamber of the spectrometer.

Chlorostannanes **1a–1f** [6,7], tributylstannane [19], and vinylsilane [1] were prepared as previously reported. Triphenylstannane and ethoxyethylether were purchased from Janssen or Aldrich.

3.1. Preparation of vinylstannanes 2

The apparatus already described for the reduction of phosphonates [9] was used. Ethoxyethylether was purified by refluxing it over, and distilling from, sodium/benzophenone under reduced pressure (10^{-1} mbar). The flask containing the reducing mixture (5 mmol of $LiAlH_4$ in 20 ml of ethoxyethylether) was fitted to the vacuum line, cooled to 0°C and degassed. Then, the chloro(vinyl)stannane **1** (3 mmol in 5 ml of ethoxyethylether) was slowly added with a cannula through the septum. During and after the addition ethoxyethylether was carriedaway into a cold trap (−60°C) and vinylstannane **2** was condensed onto a cold finger (−196°C). A solvent can be added at this step. When the reaction was complete (30 min, the cold finger was disconnected from the vacuum line by stopcocks; the apparatus was then filled with dry nitrogen on and the liquid nitrogen was subsequently removed from the top. The product was collected in a Schlenk flask and characterized by IR and NMR spectroscopy and HRMS.

3.1.1. Ethenylstannane (2a)

Yield 60%, b.p. (0.1 mbar) ≈ −110°C ^{1}H NMR (300 MHz, C_6D_6, room temperature): δ 4.64 (dd, 3H, $^{3}J_{HH}$ = 2.3 Hz, $^{4}J_{HH}$ = 1.0 Hz); 5.65 (dd, 1H, $^{3}J_{HHtrans}$ = 19.4 Hz, $^{2}J_{HH}$ = 3.8 Hz); 6.00 (ddq, 1H, $^{3}J_{HHcis}$ = 13.3 Hz, $^{2}J_{HH}$ = 3.8 Hz, $^{4}J_{HH}$ = 1.0 Hz); 6.11 (ddq, 1H, $^{3}J_{HHtrans}$ = 19.4 Hz, $^{3}J_{HHcis}$ = 13.3 Hz, $^{3}J_{HH}$ = 2.3 Hz). ^{13}C NMR (75.5 MHz, C_6D_6, room temperature): δ 129.1 (d, $^{1}J_{CH}$ = 160.2 Hz, $^{1}J^{119}_{Sn^{13}C}$ = 531.9 Hz (d)); 138.2 (t, $^{1}J_{CH}$ = 155.1 Hz). ^{119}Sn NMR (111 MHz, C_6D_6, room temperature): δ −360.7 (qdt, $^{1}J_{SnH}$ = 1917.3 Hz, $^{3}J_{SnH}$ = 204 Hz, $^{3}J^{119}_{SnH}$ = 108.5 Hz). IR (gas room temperature) (cm^{-1}): $\nu_{=C-H}$, (3042 (m), 2980 (s), 2938 (m), ν_{Sn-H}: 1865 (vs), 1250 (s). HRMS: calc. for $C_2H_5^{120}Sn$ $(M-H)^+$: 148.9413; Found: 148.942. MS (m/z) (%): 149 (19.1); 148 (7.2); 147 (15.8); 146 (6.1); 145 (14.2); 143 (6.2); 125 (8.8); 124 (10.8); 123 (29.2); 122 (51.3); 121 (54.5); 120 (100); 119 (80.3); 118 (62.3); 117 (28.8); 116 (25.4).

3.1.2. Diethenylstannane (2b)

Yield: 67% bp (0.1 mbar) ≈ −90°C. ^{1}H NMR (300 MHz, C_6D_6, room temperature): δ 5.36 (ttt, 2H, $^{3}J_{HH}$ = 2.2 Hz, $^{4}J_{HH}$ = 1.0 Hz, $^{4}J_{HH}$ = 0.6 Hz); 5.70 (ddt, 2H, $^{3}J_{HHtrans}$ = 20.0 Hz, $^{2}J_{HH}$ = 3.4 Hz, $^{4}J_{HH}$ = 0.6 Hz); 6.08 (ddt, 2H, $^{3}J_{HHcis}$ = 13.5 Hz, $^{2}J_{HH}$ = 3.4 Hz, $^{4}J_{HH}$ = 1.0 Hz); 6.24 (ddt, 2H, $^{3}J_{HHtrans}$ = 20.0 Hz, $^{3}J_{HHcis}$ = 13.5 Hz, $^{3}J_{HH}$ = 2.2 Hz). ^{13}C NMR (75.5 MHz, C_6D_6, room temperature): δ 134.2 (d, $^{1}J_{CH}$ = 153.4 Hz; $^{1}J^{119}_{SnC}$ = 519.2 Hz (d)); 136.7 (t, $^{1}J_{CH}$ = 155.7 Hz). ^{119}Sn NMR (111 MHz, C_6D_6, room temperature): δ −263.3 (tttt, $^{1}J^{119}_{SnH}$ = 1918.3 Hz, $^{2}J^{119}_{SnH}$ = 201.3 Hz, $^{3}J^{119}_{SnH}$ = $^{3}J^{119}_{SnH}$ = 98.8 Hz). IR (gas, room temperature) (cm^{-1}): $\nu_{=C-H}$: 3039 (s), 2975 (s), 2932 (s), ν_{Sr-H}: 1855 (vs), 1242 (s), 1053 (m). HRMS: calc. for $C_4H_7^{120}Sn$ $(M-H)^+$: 174.9570; Found: 174.958). MS (m/z) (%): 151 (5.8); 149 (26.6); 148 (15.2); 147 (35.1); 146 (18.8); 145 (28.2); 144 (12.0); 125 (7.8); 124 (19.9); 123 (16.3); 122 (42.2); 121 (70.7); 120 (100); 119 (78.1); 118 (81.3); 117 (35.5); 116 (29.1).

3.1.3. Triethenylstannane (2c)

Yield 74%. b.p. (0.1 mbar) ≈ −70°C. ^{1}H NMR (300 MHz, C_6D_6, room temperature): δ 5.89 (m, 1H, $^{3}J_{HH}$ = 1.7 Hz); 5.75 (dd, 3H, $^{3}J_{HHtrans}$ = 20.2 Hz, $^{2}J_{HH}$ = 3.4 Hz); 6.13 (dd, 3H, $^{3}J_{HHcis}$ = 13.6 Hz, $^{2}J_{HH}$ = 3.4 Hz); 6.32 (ddd, 3H, $^{3}J_{HHcis}$ = 13.6 Hz, $^{3}J_{HHtrans}$ = 20.2 Hz, $^{3}J_{HH}$ = 1.7 Hz). ^{13}C NMR (75.5 MHz, C_6D_6, room temperature): δ 134.2 (d, $^{1}J_{CH}$ = 152.9 Hz, $^{1}J_{SnC}$ = 516.4 Hz (d)); 136.7 (t, $^{1}J_{CH}$ = 157.4 Hz), ^{119}Sn NMR (111 MHz, C_6D_6, room temperature): δ − 199.4 (dqhept, $^{1}J_{SnH}$ = 1948.0 Hz, $^{3}J_{SnH}$ = 223.3 Hz, $^{3}J_{SnH}$ ≈ $^{2}J^{119}_{SnH}$ = 96.3 Hz). IR (gas, room temperature) (cm^{-1}): $\nu_{=C-H}$ 3040 (s), 2970 (vs), 2928 (vs), 2862 (w), ν_{Sn-H} 1855 (vs), 1388 (vs), 1060 (m), HRMS: calc. for $C_6H_9^{120}Sn$ (M −

H)$^+$: 200.9726; Found: 200.973. MS (m/z) (%): 175. (13.6); 174 (7.2); 171 (7.6); 151 (11.5); 149 (26.5); 148 (29.2); 145 (50.1); 144 (18.8); 143 (22.7); 141 (5.1); 125 (5.7); 124 (15.3); 123 (12.7); 122 (17.3); 121 (45.1); 120 (100); 119 (54.6); 118 (71.4); 117 (25.8); 116 (42.8).

3.1.4. Dimethyl(ethenyl)stannane (2d)

Yield 75%, b.p. (0.1 mbar) ≈ −80°C. ^{1}H NMR (300 MHz, C_6D_6, room temperature): δ 0.08 (d, 6H, $^3J_{HH}$ = 2.3 Hz); 4.85 (m, 1H); 5.68 (dd, 1H, $^3J_{HHtrans}$ = 20.6 Hz, $^2J_{HH}$ = 3.3 Hz, $^4J_{HH}$ = 0.7 Hz); 6.11 (ddd, 1H, $^3J_{HHcis}$ = 13.7 Hz, $^2J_{HH}$ = 3.3 Hz); 6.44 (ddd, $^3J_{HHtrans}$ = 20.6 Hz, $^3J_{HHcis}$ = 13.7 Hz, $^3J_{HH}$ = 1.5 Hz). ^{13}C NMR (75.5 MHz, C_6D_6, room temperature): δ − 12.0 (q, $^4J_{CH}$ = 129.6 Hz, $^1J_{SnC}$ = 365.0 Hz (d)); 134.6 (d, $^1J_{CH}$ = 152.2 Hz, $^1J_{SnC}$ = 477.0 Hz (d)); 136.6 (t, $^1J_{CH}$ = 147.4 Hz). ^{119}Sn NMR (111 MHz, C_6D_6, room temperature): δ − 133.7 (ddddhept, $^1J_{SnH}$ = 1798.5 Hz, $^3J_{SnH}$ ≈ $^4J_{SnH}$ ≈ 92 Hz, $^3J_{SnH}$ ≈ 175 Hz $^2J^{119}_{SnH}$ = 57.8 Hz). IR (gas, room temperature) (cm^{-1}): $\nu_{=C-H}$: 3039 (s), 2970 (vs), 2928 (vs), 2862 (w), ν_{Sn-H}: 1830 (vs) HRMS: calc. for $C_4H_9^{120}Sn$ (M − H)$^+$: 176.9726; Found: 176.973. MS (m/z) (%): 163 (11.4); 161 (8.0); 151 (21.8); 150 (13.8); 149 (17.6); 148 (10.8); 146 (8.2); 141 (6.4); 139 (9.1); 137 (52.7); 136 (33.9); 135 (100); 134 (42.7); 133 (57.6); 132 (27.8); 131 (23.5); 121 (12.6); 120 (37.0); 119 (17.8); 118 (14.8); 117 (12.7); 116 (12.7).

3.1.5. 2-Propenylstannane (2e)

Yield 66%. b.p. (0.1 mbar) ≈ −90°C. ^{1}H NMR (300 MHz, C_6D_6, room temperature): δ 2.02 (td, 3H, $^4J_{HH}$ ≈ $^4J_{HH}$ = 1.6 Hz); 4.76 (d, 3H, $^4J_{HH}$ = 1.3 Hz); 5.25 (m, 1H, $^2J_{HH}$ = 2.4 Hz, $^4J_{HH}$ = 1.6 Hz, $^4J_{HH}$ = 1.3 Hz); 5.75 (m, 1H, $^4J_{HH}$ = 1.6 Hz, $^2J_{HH}$ = 2.4 Hz) ^{13}C NMR (75.5 MHz, C_6D_6, room temperature): δ 6.0 (q, $^1J_{CH}$ = 127.0 Hz, $^2J_{SnC}$ = 415.9 Hz (d)); 130.2 (t, $^1J_{CH}$ = 155.6 Hz, $^2J_{SnC}$ = 42.2 Hz (d)); 142.1 ($^1J_{SnC}$ = 477.0 Hz (d)). ^{119}Sn NMR (111 MHz, C_6D_6, room temperature): δ − 346.9 (qdd, $^1J_{SnH}$ = 1882.0 Hz, $^3J_{SnH}$ = 185.6 Hz, $^3J_{SnH}$ = 87 Hz). IR (C_6H_6, room temperature) (cm^{-1}): $\nu_{=C-H}$ 3050 (s), 2970 (vs), 2928 (vs), 2862 (w), ν_{Sn-H} 1865 (vs), $\nu_{C=C}$ 1620 (w). HRMS: calc. for $C_3H_7^{120}Sn$ (M − H)$^+$: 162.9570; Found: 162.956. MS (m/z) (%): 163 (15.3); 162 (5.3); 161 (11.6); 159 (7.6); 135 (5.2); 125 (6.8); 124 (13.6); 123 (21.3); 122 (33.8); 121 (44.8); 120 (94.9); 119 (60.9); 118 (66.6); 117 (28.3); 116 (28.4) MIKE spectrum of m/z 163: 161, 134, 121. CAD-MIKE spectrum of m/z 163: 161, 134, 121.

3.1.6. (Z + E)-Prop-1-enylstannane (2f)

Z/E ratio 3:1. Yield 64% b.p. (0.1 mbar) ≈ −90°C. (Z) ^{1}H NMR (300 MHz, C_7D_8, room temperature): δ 1.78 (d, 3H, $^3J_{HH}$ = 6.5 Hz); 4.48 (d, 3H, $^3J_{HH}$ = 2.7 Hz); 5.78 (dm, 1H, $^3J_{HHcis}$ = 12.1 Hz); 6.56 (dq, 1H, $^3J_{HHcis}$ = 12.1 Hz, $^3J_{HH}$ = 6.5 Hz). ^{13}C NMR (75.5 MHz, C_7D_8, room temperature): δ 22.2 (q, $^1J_{CH}$ = 126.3 Hz; 119.4 (d, $^1J_{CH}$ = 153.0 Hz, $^1J_{SnC}$ = 515.3 Hz (d)), 146.2 (d, $^1J_{CH}$ = 150.1 Hz). ^{119}Sn NMR (111 MHz, C_6D_6, room temperature): δ − 418.9 ($^1J_{SnH}$ = 1896.0 Hz). (E) ^{1}H NMR (300 MHz, C_7D_8, room temperature): δ 1.84 (d, 3H, $^3J_{HH}$ = 6.1 Hz); 4.65 (d, 3H, $^3J_{HH}$ = 2.2 Hz); 5.82 (dm, 1H, $^3J_{HHtrans}$ = 18.3 Hz); 6.18 (dq, 1H, $^3J_{HHtrans}$ = 18.3 Hz, $^3J_{HH}$ = 6.1 Hz). ^{13}C NMR (75.5 MHz, C_7D_8, room temperature): δ 22.3 (q, $^1J_{CH}$ = 126.3 Hz), 119.1 (d, $^1J_{CH}$ = 153.0 Hz); 148.9 (d, $^1J_{CH}$ = 156.2 Hz); ^{119}Sn NMR (111 MHz, C_6D_6, room temperature): δ − 362.3 ($^1J_{SnH}$ = 1896.2 Hz). IR (gas, room temperature) (cm^{-1}): $\nu_{=C-H}$ 3062 (s), 2970 (vs), 2928 (vs), 2862 (w), ν_{Sn-H} 1840 (vs), $\nu_{C=C}$ 1600 (w). HRMS: calc. for $C_3H_7^{120}Sn$ (M − H)$^+$: 162.9570; Found: 162.956. MS (m/z) (%): 163 (23.3); 162 (7.5); 161 (17.2); 160 (6.3); 159 (10.6); 151 (5.4); 135 (7.9); 133 (7.5); 125 (11.6); 124 (15.6); 123 (30.7); 122 (31.2); 121 (57.9); 120 (100); 119 (62.5); 118 (82.5); 117 (49.1); 116 (37.4). MIKE spectrum of m/z 163: 161, 136, 134, 123, 121. CAD-MIKE spectrum of m/z 163: 161, 134, 123, 121.

3.2. Chloro(diethenyl)stannane (2g)

In a 5-mm NMR tube, a solution of stannane **2b** in octadeuterotoluene was prepared as reported above and cooled to −30°C. A stoichiometric amount of dichlorostannane **1b** was added and the mixture was shaken at room temperature until only the signals of stannane **2g** were observed by ^{1}H NMR spectroscopy. Yield 65%. ^{1}H NMR (300 MHz, C_7D_8, room temperature): δ 5.78 (dd, 2H, $^3J_{HHtrans}$ = 19.1 Hz, $^2J_{HH}$ = 3.3 Hz); 6.08 (dd, 2H, $^3J_{HHcis}$ = 13.0 Hz, $^2J_{HH}$ = 3.3 Hz); 6.13 (ddd, 2H, $^3J_{HHtrans}$ = 19.1 Hz, $^3J_{HHcis}$ = 13.0 Hz, $^3J_{HH}$ = 3.2 Hz); 7.24 (m, 1H, $^3J_{HH}$ = 3.2 Hz). ^{13}C NMR (75.5 MHz, C_7D_8, room temperature): δ 135.3 (d, $^1J_{CH}$ = 154.7 Hz, $^1J_{SnC}$ = 603.0 Hz (d)); 138.0 (t, $^1J_{CH}$ = 158.7 Hz). ^{119}Sn NMR (111 MHz, C_6D_6, room temperature): δ −88.9 ($^1J_{SnH}$ = 2501.0 Hz). HRMS: calc. for $C_4H_6^{35}Cl^{120}Sn$ (M − H)$^+$: 208.9180; Found: 208.918. MS (m/z) (%): 209 (12.6); 208 (4.9); 207 (9.1); 182 (23.2); 181 (5.8); 178 (8.2); 175 (9.1); 173 (6.0); 155 (24.4); 153 (15.6); 151 (14.9); 149 (26.3); 148 (23.9); 147 (51.0); 146 (36.0); 145 (39.4); 121 (38.7); 120 (96.0); 119 (53.9); 118 (75.8); 117 (38.7); 116 (37.9).

3.3. (2-Chloromethyl)-1-bromocyclopropane (4b)

Into a two-necked flask was introduced under dinitrogen a solution of stannane **2c** (23 mmol) in diethyl ether (20 ml). 2-(Chloromethyl)-1,1-dibromocyclopropane **4a** [21] (5.0 g, 20 mmol) in degassed diethyl ether (10 ml) was slowly added and the mixture was stirred for 4 h at room temperature. The solution was then poured onto a saturated solution of ammonium chloride (5 ml). The organic phase was separated and the

aqueous phase was washed three times with CH_2Cl_2. Distillation in vacuo led to pure **4b** (yield 72%).

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