

Note

# Synthesis of (*Z*)-1-aryl-2-(germyl)-1-(stannyl)ethenes and the related ethenes, precursors to stereodefined germylethenes, via Pd(dba)<sub>2</sub>–P(OCH<sub>2</sub>)<sub>3</sub>CEt-catalyzed germastannation of acetylenes in THF

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## Abstract

(*Z*)-1-Aryl-2-(germyl)-1-(stannyl)ethenes are synthesized in high yields by the addition of tributyl(triethylgermyl)stannane to arylacetylenes catalyzed by a specific combination catalyst, Pd(dba)<sub>2</sub> and 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane, in tetrahydrofuran. Ethynylthiophene and 2-methyl-3-butyn-2-ol are also subject to the germastannation to afford the respective adducts in high yields. In addition, the  $J_{\text{Sn-H}}$  and <sup>13</sup>C-NMR data for their adducts are presented. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Germylstannane; Acetylenes; Germastannation; (*Z*)-Germyl(stannyl)ethenes; Palladium catalysis

## 1. Introduction

The bis-silylation [1], bis-germylation [2], silastannation [3] or bis-stannation [4] of acetylenes forming new sp<sup>2</sup>carbon–silicon, sp<sup>2</sup>carbon–germanium or sp<sup>2</sup>carbon–tin bonds has been reported. The importance of their products is the possibility of transforming them to other new derivatives through the reactions such as Kosugi Migita-Stille coupling [5]. For example, the demetallations such as the desilylation of silylethenes [3f], the destannylation of stannylethenes [3g] and carbon–carbon formation by the cross couplings using silylethenes [6] or stannylethenes [5] have been reported. In all these cases, the reaction proceeds with the retention of the configuration, except for an example using *vicinal* di(silyl)ethenes [6f]. Recently, much attention has been focused on the germylethene

derivatives, because pyridyl(germyl)ethene was reported to undergo [2 + 3] cycloaddition with nitrile oxide to produce (germyl)isoxazolines possessing vasodilating, antithrombotic and cardioprotective activity [7]. To synthesize such isoxazolines with a stereodefined structure, the use of stereodefined germylethene derivatives is essential. The germastannation of triple bonds can provide precursors to a variety of stereodefined vinylgermane derivatives through the destannylation [3g] or the Kosugi Migita-Stille coupling [5]. For the germastannation of acetylenes, Piers et al. [8] previously reported that addition of tributyl(trimethylgermyl)stannane to nonterminal  $\alpha,\beta$ -acetylenic esters in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> gave a mixture of *vicinal* (germyl)stannylethenes with (*E*) and (*Z*)-configurations. Mitchell et al. investigated the addition of the (germyl)stannane to terminal alkynes including phenylacetylene catalyzed by Pd(PPh<sub>3</sub>)<sub>4</sub> and reported that the reaction formed *vicinal* (germyl)stannylethenes with the *Z*-configuration [9]. However the product yields did not exceed 50%.

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Table 1  
Influence of catalysts and reaction conditions in Scheme 1<sup>a</sup>

Run	Catalyst	Ligand	Solvent <sup>b</sup>	Reaction time (h)	Yield (%) <sup>c</sup>
1	Pd(PPh <sub>3</sub> ) <sub>4</sub>	–	–	19	5
2	Pd(dba) <sub>2</sub>	–	–	48	0
3	Pd(dba) <sub>2</sub>	P( <i>o</i> -tol) <sub>3</sub> <sup>d</sup>	–	48	2
4	Pd(dba) <sub>2</sub>	P(OPh) <sub>3</sub> <sup>d</sup>	–	48	0
5	Pd(dba) <sub>2</sub>	P(OEt) <sub>3</sub> <sup>d</sup>	–	96	0
6	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	–	–	48	0
7	RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub>	–	–	48	0
8	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	–	THF	40	Trace
9	PtCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	–	–	48	0
10	Pd(dba) <sub>2</sub>	PPh <sub>3</sub> <sup>d</sup>	–	48	27
11 <sup>c</sup>	Pd(dba) <sub>2</sub>	PPh <sub>3</sub>	THF	48	32
12	Pd(dba) <sub>2</sub>	P(OCH <sub>2</sub> ) <sub>3</sub> CEt <sup>d</sup>	THF	48	91
13	Pd(dba) <sub>2</sub>	P(OCH <sub>2</sub> ) <sub>3</sub> CEt <sup>d</sup>	PhH	48	0

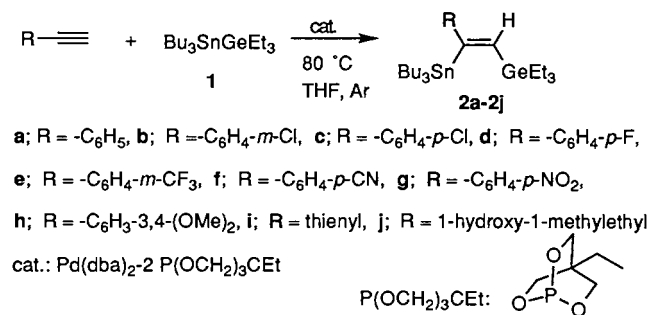
<sup>a</sup> A 1 mmol:2 mmol:0.01 mmol mixture of **1**, phenylacetylene and the catalyst was introduced into a glass ampoule and degassed through several freeze-evacuate-thaw cycles prior to sealing under vacuum. The mixture was then stirred at 80°C.

<sup>b</sup> One ml of the solvent was used.

<sup>c</sup> GLC yields based on the **1** used.

<sup>d</sup> Amounts of the ligand were 0.02 mmol.

<sup>e</sup> Amounts of the palladium and the ligand were 0.05 and 0.1 mmol, respectively.



Scheme 1.

As mentioned above, in view of the importance for the (*Z*)-(germyl)stannylethenes as key compounds to synthesize stereodefined germylethene derivatives, we examined the addition of tributyl(trimethylgermyl)stannane **1** to phenylacetylene in the presence of a transition metal complex catalyst and found that a specific palladium combination catalyst, Pd(dba)<sub>2</sub>-P(OCH<sub>2</sub>)<sub>3</sub>CEt (dba = dibenzylideneacetone, P(OCH<sub>2</sub>)<sub>3</sub>CEt = 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane<sup>2</sup>), very effectively accelerated the germastannation in tetrahydrofuran (THF) to afford (*Z*)-2-(germyl)-1-phenyl-1-(stannyl)ethenes in a high-isolated yield. We now report an alternative synthesis of (*Z*)-1-aryl-2-(germyl)-1-(stannyl)ethenes as precursors to a variety of

germylethene derivatives and related (*Z*)-(germyl)stannylethenes by the reaction shown in Scheme 1.

## 2. Results and discussion

The Pd(PPh<sub>3</sub>)<sub>4</sub>-catalyzed addition of **1** to phenylacetylene was carried out at 80°C for 19 h in a sealed glass ampoule tube. However, the reaction produced (*Z*)-1-(tributylstannyl)-2-(triethylgermyl)-1-phenylethene (**2a**) in only 5% (entry 1 in Table 1). These results suggest that the reactivity of **1** is much lower than that of the tributyl(trimethylgermyl)stannane previously used by Mitchell et al. The reaction conditions are almost the same as those reported by Mitchell et al. [9] except for the reaction time and the use of **1**. Promising results were obtained using Pd(dba)<sub>2</sub> with two equivalents of triphenylphosphine without or with THF as the solvent. The catalyst showed a slightly better activity for producing the product **2a** in 27% and 32% yield, respectively (entries 10 and 11). Much better results were obtained using a combination catalyst of Pd(dba)<sub>2</sub> and the phosphite ligand, 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane, **L**. The catalyst system most effectively accelerated the reaction, especially in THF, to realize the highest product yield (91%, entry 12) of the adduct **2a**. Other catalysts such as Pd(dba)<sub>2</sub>, Pd(dba)<sub>2</sub>-2P(*o*-tol)<sub>3</sub> (*o*-tol = *o*-tolyl), Pd(dba)<sub>2</sub>-2P(OPh)<sub>3</sub>, Pd(dba)<sub>2</sub>-2P(OEt)<sub>3</sub>, RhCl(PPh<sub>3</sub>)<sub>3</sub>, RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, and PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> were all ineffective (entries 2–9). Here, the use of THF is essential in the present germastannation. No reaction occurred when an aromatic solvent such as benzene was used (entry 13).

<sup>2</sup> P(OCH<sub>2</sub>)<sub>3</sub>CEt; 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane. For use of the specific ligand in the Pd-catalyzed addition of Si–Si bonds and Ge–Ge bonds to acetylenes in benzene solvent, see: (the former) [1f]; (the latter) [2a,b].

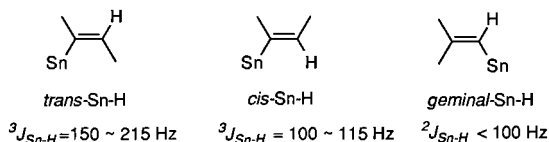


Fig. 1. Reported  $J_{\text{Sn-H}}$  in three different types of vinylstannanes.

The NMR coupling constants ( $J_{\text{Sn-H}}$ ) for the respective tin-117 and 119 with vinyl proton for adduct **2a** were 161.2 and 168.4 Hz, respectively, being typical for the structures with tin and hydrogen in *trans*-disposition [3b,3e,3f,4b,9]. The coupling constants of  $^3J_{\text{Sn-H}}(\text{trans})$ ,  $^3J_{\text{Sn-H}}(\text{cis})$ , and  $^2J_{\text{Sn-H}}(\text{geminal})$  for the tri-substituted or di-substituted stannylethene derivatives have been reported [3b,3e,3f,4b,9] and are summarized in Fig. 1.

Next, the present catalyst system was applied to the reaction with a series of arylacetylenes. Respective (*Z*)-1-aryl-1-(tributylstannyl)-2-(triethylgermyl)ethenes were successfully synthesized in satisfactory yields, as shown in Table 2. The observed magnitudes of  $^3J_{\text{Sn-H}}$  for their products are summarized in Table 3.

By reference to the magnitudes of the reported  $J_{\text{Sn-H}}$  shown in Fig. 1, the configurations for **2b** through **2h** were determined as the (*Z*)-structure, in which a stannyl group is connected with the  $\text{sp}^2$  carbon bearing an aryl group.

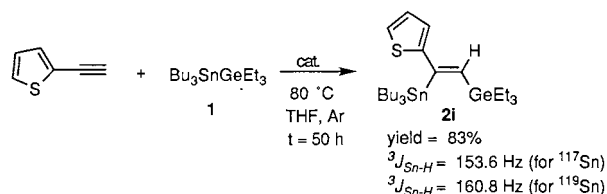
The germastannation of 2-ethynylthiophene also gave (*Z*)-1-(tributylstannyl)-2-(triethylgermyl)-1-(2-thienyl)ethene **2i** in the isolated yield of 83% (Scheme 2). The reaction in Scheme 3 showed that the hydroxy functional group was tolerated during the reaction. Thus, 2-methyl-3-butyn-2-ol was effectively subject to the germastannation to produce (*Z*)-3-(tributylstannyl)-4-(triethylgermyl)-2-methyl-3-buten-2-ol (**2j**) in 85% yield.

The coupling constants,  $^3J_{\text{Sn-H}}$ , of **2j** (179.0 and 187.7 Hz) possessing the electron-donating group (1-hydroxy-

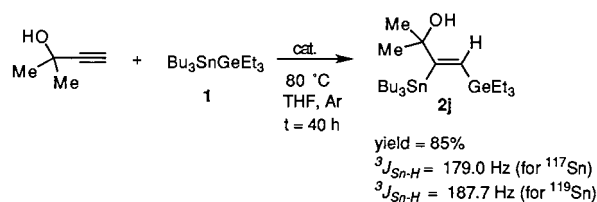
Table 3  
 $J_{\text{Sn-H}}$  for (*Z*)-Ar(Bu<sub>3</sub>Sn)C=CH(GeEt<sub>3</sub>)<sup>a</sup>

Run	Product	Substituent (X)	$^3J_{117\text{Sn-H}}$	$^3J_{119\text{Sn-H}}$
1	<b>2a</b>	H	161.2	168.4
2	<b>2b</b>	<i>m</i> -Cl	156.0	163.2
3	<b>2c</b>	<i>p</i> -Cl	157.2	164.8
4	<b>2d</b>	<i>p</i> -F	159.2	166.4
5	<b>2e</b>	<i>m</i> -CF <sub>3</sub>	154.8	162.0
6	<b>2f</b>	<i>p</i> -CN	151.2	158.4
7	<b>2g</b>	<i>p</i> -NO <sub>2</sub>	150.0	156.8
8	<b>2h</b>	3,4-(OMe) <sub>2</sub>	162.4	169.6

<sup>a</sup> Average of three measurements in CDCl<sub>3</sub> is shown in Hz.



Scheme 2.



Scheme 3.

1-methylethyl group) on tin-bearing vinyl carbon were reasonably the smallest among adducts obtained in this study.

In Table 4 are shown selected NMR data for all adducts **2a–2j**. In a series of 1-aryl-2-germyl-1-stan-

Table 2  
Reaction time and product yields in the reaction of **1** with arylacetylenes<sup>a</sup>

Run	Time (h)	Conversion of <b>1</b>	Substituent (X)	Product number	Yield (%) <sup>b</sup>
1 <sup>c</sup>	19	98	H	<b>2a</b>	91 <sup>d</sup>
2	50	98	H	<b>2a</b>	85
3	30	94	<i>m</i> -Cl	<b>2b</b>	88
4	19	91	<i>p</i> -Cl	<b>2c</b>	78
5	40	95	<i>p</i> -F	<b>2d</b>	75
6	30	94	<i>m</i> -CF <sub>3</sub>	<b>2e</b>	83
7	40	88	<i>p</i> -CN	<b>2f</b>	76
8	40	96	<i>p</i> -NO <sub>2</sub>	<b>2g</b>	91
9	35	98	3,4-(OMe) <sub>2</sub>	<b>2h</b>	78

<sup>a</sup> A THF (5 ml) solution of 1 mmol:3–4 mmol:0.05 mmol:0.1 mmol of **1**, arylacetylene, Pd(dba)<sub>2</sub> and phosphite **L** was stirred at 80°C.

<sup>b</sup> Isolated yields after column chromatography (see Section 3) unless otherwise stated. The chromatography produced a spectroscopically (<sup>1</sup>H-NMR) pure product.

<sup>c</sup> See footnote 'a' in the Table 1.

<sup>d</sup> GLC yield based on the **1** used.

Table 4  
Selected NMR data for (*Z*)-R(Bu<sub>3</sub>Sn)C=CH(GeEt<sub>3</sub>)

Run	Product	Substituent (R)	$\delta(\text{=CH})^a$	$\delta(\text{C}^1)^b$	$\delta(\text{C}^2)^b$
1	<b>2a</b>	C <sub>6</sub> H <sub>5</sub>	6.63	165.5	151.8
2	<b>2b</b>	<i>m</i> -ClC <sub>6</sub> H <sub>4</sub>	6.63	164.2	153.6
3	<b>2c</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	6.62	164.3	150.3
4	<b>2d</b>	<i>p</i> -FC <sub>6</sub> H <sub>4</sub>	6.61	164.4	147.9
5	<b>2e</b>	<i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	6.67	164.3	152.4
6	<b>2f</b>	<i>p</i> -CNC <sub>6</sub> H <sub>4</sub>	6.65	164.2	156.6
7	<b>2g</b>	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	6.69	164.0	158.9
8	<b>2h</b>	3,4-(OMe) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	6.63	164.9	148.2
9	<b>2i</b>	2-thienyl	6.93	155.1	154.5
10	<b>2j</b>	C(CH <sub>3</sub> )OHCH <sub>3</sub>	6.42	175.1	135.7

<sup>a</sup> NMR was measured in chloroform-*d* and chemical shifts referenced to TMS in ppm

<sup>b</sup> C<sup>1</sup> is the tin-bearing vinyl carbon, while C<sup>2</sup> bears germanium. Both are shown with reference to TMS.

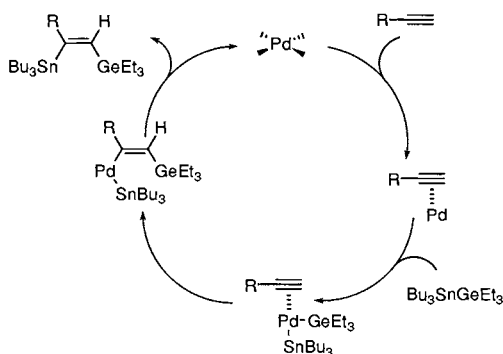


Fig. 2. A possible mechanism for the formation of (*Z*)-2-(germyl)-1-(stannyl)ethenes.

nylethenes, the chemical shifts of the germanium-bearing vinyl carbon (C<sup>2</sup> in the Table 4) were affected by the electronic effects of the substituent on the aromatic ring. In contrast, C<sup>1</sup> was not subject to such a large change. Similar propensities are seen in the NMR data for vicinal (stannyl)silylethenes [3e].

We further examined the present catalyst system for other alkynols such as 2-propyn-1-ol, 5-hexyn-1-ol and 4-pentyn-2-ol. However, the germastannation did not occur, apart from that of 4-pentyn-2-ol, which gave a 17% yield of the expected (*Z*)-adduct. Nonterminal alkynes such as 2-butyne-1,4-diol and terminal acetylenes such as 1-hexyne, (trimethylsilyl)phenylethyne, and (dimethylphenylsilyl)phenylethyne also did not enter into the germastannation. Further study is needed for these acetylenes.

Aimed at better understanding the reaction mechanism, the reaction of Pd(dba)<sub>2</sub> with **1** in THF in the presence of ligand **L** was examined at 80°C for 40 h under argon. However, the attempt left **1** unchanged, and demonstrated that a germyl(stannyl)palladium was not formed under these conditions. Therefore, the first step for this reaction may be coordination of an acety-

lene to the palladium, although we can not entirely exclude the possibility of the initial addition of a germylstannane to the palladium complex as the primary event.<sup>3</sup> Hence, we propose the mechanism shown in Fig. 2.

In conclusion, the present method provided a high-yield synthesis of (*Z*)-1-aryl-2-(germyl)-1-(stannyl)ethenes, (*Z*)-2-(germyl)-1-(stannyl)-1-(thienyl)ethenes and (*Z*)-2-(germyl)-1-[1-hydroxy-1-(substituted)alkyl]-1-(stannyl)ethenes, which can be used as starting materials for a variety of germylethene derivatives.

### 3. Experimental

#### 3.1. Measurements

GLC analyses were performed using an Ohkura Model 103 instrument equipped with a thermal conductivity detector and a stainless column packed with 20% or 10% Silicone KF-96/Celite 545 SK (60–80 mesh, 2 m × 3 mm). The IR spectra were measured using a JASCO A-102 spectrophotometer. Mass spectra were obtained using a JEOL JMSAX-500 spectrometer with the DA7000 data system. <sup>1</sup>H-NMR spectra and <sup>13</sup>C-NMR spectra were recorded at 400 MHz and 100 MHz, respectively, on a Varian UNITY-400 spectrometer in chloroform-*d* using tetramethylsilane (TMS) as the internal standard. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), sep (septet) and m (multiplet).

#### 3.2. Materials

Arylacetylenes and thienylacetylene were prepared by the Sonogashira reaction [11]. Aryl halides and 2-methyl-3-butyn-2-ol were purchased from Tokyo Kasei Kogyo Co. and used without purification. Pd(dba)<sub>2</sub> [12], RhCl(PPh<sub>3</sub>)<sub>3</sub> [13], RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> [14] and PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> [15] were prepared according to the literature procedures. Tetrakis(triphenylphosphine)palladium, triphenylphosphine, triphenylphosphite, triethylphosphite, 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane **L** and silica gel (Wako gel C-300) were purchased from Wako Chemical. Co. Tributyl(triethylgermyl)stannane was prepared by reference to the synthesis of tributyl(trimethylsilyl)stannane [16]. Benzene and toluene were distilled from LiAlH<sub>4</sub> and stored over molecular sieves. THF was distilled from sodium benzophenone ketyl prior the use.

<sup>3</sup> (a) For the addition of a Pd–Sn bond to acetylenes, see: [4d]. (b) For the addition of a Pd–Si bond to an acetylene, see: [10a]. (c) For the addition of a Pt–Si bond to an acetylene, see: [10b]. (d) For the formation of a Pt–Ge bond from a digermane and Platinum complex, see: [10c].

### 3.3. Synthesis

#### 3.3.1. A typical example for the germastannation of the acetylenes: (*Z*)-1-(tributylstannyl)-2-(triethylgermyl)-1-phenylethene (**2a**)

A THF (5 ml) solution of phenylacetylene (0.451 g, 4.4 mmol), **1** (0.456 g, 1.01 mmol), Pd(dba)<sub>2</sub> (0.0281 g, 0.049 mmol), and phosphite **L** (0.0167 g, 0.103 mmol) was stirred at 80°C under argon. After 50 h, the GLC analysis of the resulting mixture disclosed that 98% of **1** was consumed. The mixture was concentrated under vacuum and then added to the concentrate a hexane–ether (1/1) mixed solution. The resulting solution was passed through a short silica gel column with hexane–ether (1/1) to remove tarry compounds. Purification by column chromatography eluted with hexane then gave spectroscopically pure **2a** as a colorless oil (0.477 g, 85% yield based on the **1** used). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.24 (m, 2H), 7.13 (m, 2H), 6.98 (m, 1H), 6.63 (s, 1H, <sup>3</sup>J<sub>Sn–H</sub> = 161.2 (for <sup>117</sup>Sn), 168.4 (for <sup>119</sup>Sn) Hz), 1.4 (m, 6H), 1.26 (sep, 6H, *J* = 7.2 Hz), 1.07 (t, 9H, *J* = 7.6 Hz), 0.87 (m, 21H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 165.5, 151.8, 146.5, 127.9, 126.0, 125.3, 29.1, 27.4, 13.6, 11.6, 9.2, 5.6 ppm. IR (neat) 3050, 2950, 2910, 2860, 1480, 1460, 700 cm<sup>-1</sup>. LRMS (EI) 554 [M]<sup>+</sup>, 525 [M–C<sub>2</sub>H<sub>5</sub>]<sup>+</sup>, 497 [M–C<sub>4</sub>H<sub>9</sub>]<sup>+</sup>, 468 [M–C<sub>2</sub>H<sub>5</sub>–C<sub>4</sub>H<sub>9</sub>]<sup>+</sup>, 393 [M–C<sub>6</sub>H<sub>15</sub>Ge]<sup>+</sup>, 293 [M–C<sub>12</sub>H<sub>27</sub>Sn]<sup>+</sup>. HRMS (EI) Calc. for C<sub>26</sub>H<sub>48</sub>GeSn: 554.1991. Found: 554.1994.

#### 3.4. Isolation and spectral data for other new germyl(stannyl)ethenes (**2b**)–(**2j**)

##### 3.4.1. (*Z*)-1-(tributylstannyl)-1-(*m*-chlorophenyl)-2-(triethylgermyl)ethene (**2b**)

A reaction similar to that for the synthesis of **2a** was carried out. Purification of the resulting mixture by column chromatography eluted with hexane gave spectroscopically pure **2b** as a colorless oil (0.527 g, 88% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.17 (m, 1H), 7.11 (m, 1H), 6.96 (m, 1H), 6.84 (m, 1H), 6.63 (s, 1H, <sup>3</sup>J<sub>Sn–H</sub> = 156.0 (for <sup>117</sup>Sn), 163.2 (for <sup>119</sup>Sn) Hz), 1.4 (m, 6H), 1.26 (sep, 6H, *J* = 7.2 Hz), 1.07 (t, 9H, *J* = 7.8 Hz), 0.88 (m, 21H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 164.2, 153.6, 147.8, 133.7, 129.0, 126.1, 125.3, 124.3, 29.0, 27.3, 13.6, 11.6, 9.1, 5.5 ppm. IR (neat) 3050, 2950, 2925, 2870, 1585, 1460, 1070, 1020, 875, 840, 790, 740, 690 cm<sup>-1</sup>. LRMS (EI) 588 [M]<sup>+</sup>, 559 [M–C<sub>2</sub>H<sub>5</sub>]<sup>+</sup>, 531 [M–C<sub>4</sub>H<sub>9</sub>]<sup>+</sup>, 477 [M–C<sub>6</sub>H<sub>4</sub>Cl]<sup>+</sup>. HRMS (EI) Calc. for C<sub>26</sub>H<sub>47</sub>ClGeSn: 588.1600. Found: 588.1558.

##### 3.4.2. (*Z*)-1-(tributylstannyl)-1-(*p*-chlorophenyl)-2-(triethylgermyl)ethene (**2c**)

The reaction and purification were carried out with a procedure similar to the synthesis of **2b**. Spectroscopically pure **2c** was obtained as a colorless oil (0.430 g, 78% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.22 (m, 2H), 6.9 (m,

2H), 6.62 (s, 1H, <sup>3</sup>J<sub>Sn–H</sub> = 157.2 (for <sup>117</sup>Sn), 164.8 (for <sup>119</sup>Sn) Hz), 1.4 (m, 6H), 1.27 (sep, 6H, *J* = 7.6 Hz), 1.07 (t, 9H, *J* = 7.8 Hz), 0.88 (m, 21H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 164.3, 150.3, 147.5, 131.1, 127.9, 127.4, 29.0, 27.4, 13.6, 11.6, 9.1, 5.6 ppm. IR (neat) 3065, 2950, 2925, 2860, 1480, 1460, 1090, 1010, 815, 690, 645 cm<sup>-1</sup>. LRMS (EI) 588 [M]<sup>+</sup>, 559 [M–C<sub>2</sub>H<sub>5</sub>]<sup>+</sup>, 531 [M–C<sub>4</sub>H<sub>9</sub>]<sup>+</sup>, 477 [M–C<sub>6</sub>H<sub>4</sub>Cl]<sup>+</sup>. HRMS (EI) Calc. for C<sub>26</sub>H<sub>47</sub>ClGeSn: 588.1600. Found: 588.1588.

##### 3.4.3. (*Z*)-1-(tributylstannyl)-2-(triethylgermyl)-1-(*p*-fluorophenyl)ethene (**2d**)

The reaction and purification were carried out with a procedure similar to the synthesis of **2b**. Spectroscopically pure **2d** was obtained as a colorless oil (0.429 g, 75% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 6.93 (d, 4H, *J* = 7.2 Hz), 6.61 (s, 1H, <sup>3</sup>J<sub>Sn–H</sub> = 159.2 (for <sup>117</sup>Sn), 166.4 (for <sup>119</sup>Sn) Hz), 1.39 (m, 6H), 1.26 (sep, 6H, *J* = 7.2 Hz), 1.07 (t, 9H, *J* = 7.8 Hz), 0.87 (m, 21H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 164.4, 161.1 (d, <sup>1</sup>J<sub>CF</sub> = 242 Hz), 147.9, 147.1, 127.4, 114.6 (d, <sup>2</sup>J<sub>CF</sub> = 20.5 Hz), 29.0, 27.4, 13.6, 11.6, 9.1, 5.6 ppm. IR (neat) 3030, 2950, 2925, 2860, 1595, 1495, 1460, 1365, 1225, 1150, 1010, 825, 725, 690 cm<sup>-1</sup>. LRMS (EI) 572 [M]<sup>+</sup>, 543 [M–C<sub>2</sub>H<sub>5</sub>]<sup>+</sup>, 515 [M–C<sub>4</sub>H<sub>9</sub>]<sup>+</sup>, 281 [M–C<sub>12</sub>H<sub>27</sub>Sn]<sup>+</sup>. HRMS (EI) Calc. for C<sub>26</sub>H<sub>47</sub>FGeSn: 572.1869. Found: 572.1890.

##### 3.4.4. (*Z*)-1-(tributylstannyl)-2-(triethylgermyl)-1-(*m*-trifluoromethylphenyl)ethene (**2e**)

The reaction and purification were carried out with a procedure similar to the synthesis of **2b**. Spectroscopically pure **2e** was obtained as a colorless oil (0.534 g, 83% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.40 (m, 2H), 7.21 (m, 1H), 7.15 (m, 1H), 6.67 (s, 1H, <sup>3</sup>J<sub>Sn–H</sub> = 154.8 (for <sup>117</sup>Sn), 162.0 (for <sup>119</sup>Sn) Hz), 1.39 (m, 6H), 1.25 (sep, 6H, *J* = 7.2 Hz), 1.08 (t, 9H, *J* = 8 Hz), 0.88 (m, 21H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 164.3, 152.4, 148.5, 130.1 (q, <sup>2</sup>J<sub>CF</sub> = 31 Hz), 129.3, 128.3, 124.3 (q, <sup>1</sup>J<sub>CF</sub> = 270 Hz), 122.8, 122.0, 29.0, 27.3, 13.5, 11.6, 9.1, 5.6 ppm. IR (neat) 3050, 2950, 2920, 2860, 1455, 1160, 1130, 1070, 700 cm<sup>-1</sup>. LRMS (EI) 622 [M]<sup>+</sup>, 593 [M–C<sub>2</sub>H<sub>5</sub>]<sup>+</sup>, 565 [M–C<sub>4</sub>H<sub>9</sub>]<sup>+</sup>. HRMS (EI) Calc. for C<sub>27</sub>H<sub>47</sub>F<sub>3</sub>GeSn: 622.1864. Found: 622.1819.

##### 3.4.5. (*Z*)-1-(tributylstannyl)-1-(*p*-cyanophenyl)-2-(triethylgermyl)ethene (**2f**)

The reaction and purification were carried out with a procedure similar to the synthesis of **2b**. Spectroscopically pure **2f** was obtained as a colorless oil (0.436 g, 76% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.54 (m, 2H), 7.04 (m, 2H), 6.65 (s, 1H, <sup>3</sup>J<sub>Sn–H</sub> = 151.2 (for <sup>117</sup>Sn), 158.4 (for <sup>119</sup>Sn) Hz), 1.39 (m, 6H), 1.26 (sep, 6H, *J* = 7.2 Hz), 1.08 (t, 9H, *J* = 7.8 Hz), 0.88 (m, 21H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 164.2, 156.6, 149.2, 131.8, 126.7, 119.3, 108.7, 28.9, 27.3, 13.5, 11.6, 9.1, 5.5 ppm. IR (neat) 3050, 2945, 2920, 2865, 2225, 1595, 1490, 1460, 1020,

825, 690, 675  $\text{cm}^{-1}$ . LRMS (EI) 579  $[\text{M}]^+$ , 550  $[\text{M}-\text{C}_2\text{H}_5]^+$ , 522  $[\text{M}-\text{C}_4\text{H}_9]^+$ , 493  $[\text{M}-\text{C}_2\text{H}_5-\text{C}_4\text{H}_9]^+$ , 418  $[\text{M}-\text{C}_6\text{H}_{15}\text{Ge}]^+$ . HRMS (EI) Calc. for  $\text{C}_{27}\text{H}_{47}\text{NGeSn}$ : 579.1942. Found: 579.1989.

#### 3.4.6. (Z)-1-(tributylstannyl)-2-(triethylgermyl)-1-(p-nitrophenyl)ethene (**2g**)

The reaction and purification were carried out with a procedure similar to the synthesis of **2b**. Spectroscopically pure **2g** was obtained as a colorless oil (0.580 g, 91% yield).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  8.13 (m, 2H), 7.08 (m, 2H), 6.69 (s, 1H,  $^3J_{\text{Sn-H}} = 150.0$  (for  $^{117}\text{Sn}$ ), 156.8 (for  $^{119}\text{Sn}$ ) Hz), 1.40 (m, 6H), 1.26 (sep, 6H,  $J = 7.2$  Hz), 1.08 (t, 9H,  $J = 8$  Hz), 0.89 (m, 21H) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  164.0, 158.9, 149.7, 145.6, 126.6, 123.4, 29.0, 27.3, 13.5, 11.7, 9.1, 5.5 ppm. IR (neat) 3020, 2950, 2920, 2860, 1585, 1515, 1455, 1340, 1105, 1015, 860, 840, 720  $\text{cm}^{-1}$ . LRMS (EI) 599  $[\text{M}]^+$ , 570  $[\text{M}-\text{C}_2\text{H}_5]^+$ , 542  $[\text{M}-\text{C}_4\text{H}_9]^+$ . HRMS (EI) Calc. for  $\text{C}_{26}\text{H}_{47}\text{NO}_2\text{GeSn}$ : 599.1841. Found: 599.1821.

#### 3.4.7. (Z)-1-(tributylstannyl)-2-(triethylgermyl)-1-(3,4-dimethoxyphenyl)ethene (**2h**)

The reaction and purification were carried out with a procedure similar to the synthesis of **2b**. Spectroscopically pure **2h** was obtained as a colorless oil (0.478 g, 78% yield).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.73 (m, 1H), 6.63 (s, 1H,  $^3J_{\text{Sn-H}} = 162.4$  (for  $^{117}\text{Sn}$ ), 169.6 (for  $^{119}\text{Sn}$ ) Hz), 6.56 (m, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 1.42 (m, 6H), 1.27 (sep, 6H,  $J = 7.2$  Hz), 1.08 (t, 9H,  $J = 7.8$  Hz), 0.88 (m, 21H) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  164.9, 148.2, 147.0, 145.8, 144.9, 118.0, 110.9, 109.7, 55.9, 55.7, 29.1, 27.4, 13.6, 11.6, 9.1, 5.6 ppm. IR (neat) 3040, 2940, 2920, 2865, 1505, 1460, 1260, 1030, 815, 785, 700  $\text{cm}^{-1}$ . LRMS (EI) 614  $[\text{M}]^+$ , 557  $[\text{M}-\text{C}_4\text{H}_9]^+$ , 453  $[\text{M}-\text{C}_6\text{H}_{15}\text{Ge}]^+$ , 323  $[\text{M}-\text{C}_{12}\text{H}_{27}\text{Sn}]^+$ . HRMS (EI) Calc. for  $\text{C}_{28}\text{H}_{52}\text{O}_2\text{GeSn}$ : 614.2201. Found: 614.2225.

#### 3.4.8. (Z)-1-(tributylstannyl)-2-(triethylgermyl)-1-(2-thienyl)ethene (**2i**)

The reaction and purification were carried out with a procedure similar to the synthesis of **2b**. Spectroscopically pure **2i** was obtained as a colorless oil (0.470 g, 83% yield).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.06 (m, 1H), 6.93 (s, 1H,  $^3J_{\text{Sn-H}} = 153.6$  (for  $^{117}\text{Sn}$ ), 160.8 (for  $^{119}\text{Sn}$ ) Hz), 6.91 (m, 1H), 6.67 (m, 1H), 1.46 (m, 6H), 1.3 (sep, 6H,  $J = 7.2$  Hz), 1.07 (t, 9H,  $J = 7.8$  Hz), 0.99 (m, 6H), 0.89 (m, 15H) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  155.1, 154.5, 147.7, 126.8, 122.9, 29.0, 27.3, 13.6, 11.9, 9.1, 5.8 ppm. IR (neat) 3060, 2950, 2925, 2870, 1505, 1455, 1420, 1375, 1220, 1070, 1015, 810, 680  $\text{cm}^{-1}$ . LRMS (EI) 560  $[\text{M}]^+$ , 531  $[\text{M}-\text{C}_2\text{H}_5]^+$ , 503  $[\text{M}-\text{C}_4\text{H}_9]^+$ , 269  $[\text{M}-\text{C}_{12}\text{H}_{27}\text{Sn}]^+$ . HRMS (EI) Calc. for  $\text{C}_{24}\text{H}_{47}\text{SGeSn}$ : 560.1554. Found: 560.1540.

#### 3.4.9. (Z)-3-(tributylstannyl)-4-(triethylgermyl)-2-methyl-3-buten-2-ol (**2j**)

The reaction was carried out with a procedure similar to the synthesis of **2a**. Purification of the resulting mixture by column chromatography eluted with dichloromethane spectroscopically gave pure **2j** as a colorless oil (0.461 g, 85% yield).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.42 (s, 1H,  $^3J_{\text{Sn-H}} = 179.0$  (for  $^{117}\text{Sn}$ ), 187.7 (for  $^{119}\text{Sn}$ ) Hz), 1.51 (s, 1H), 1.47 (m, 6H), 1.33 (sep, 6H,  $J = 7.2$  Hz), 2.39 (s, 6H), 1.03 (t, 9H,  $J = 7.8$  Hz), 0.88 (m, 21H) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  175.1, 135.7, 78.0, 30.6, 29.3, 27.6, 13.7, 12.6, 9.1, 5.9 ppm. IR (neat) 3600, 3450, 2950, 2920, 2865, 1460, 1375, 1260, 1100, 1020, 835, 710  $\text{cm}^{-1}$ . LRMS (EI) 536  $[\text{M}]^+$ , 518  $[\text{M}-\text{H}_2\text{O}]^+$ , 477  $[\text{M}-\text{C}_3\text{H}_7\text{O}]^+$ . HRMS (EI) Calc. for  $\text{C}_{23}\text{H}_{50}\text{OGeSn}$ : 536.2095. Found: 536.2064.

#### 3.5. The reaction of $\text{Pd}(\text{dba})_2-2\text{P}(\text{OCH}_2)_3\text{CEt}$ with $(\text{Et}_3\text{Ge})\text{SnBu}_3$ at $80^\circ\text{C}$ in THF

A THF (1 ml) solution of  $\text{Pd}(\text{dba})_2$  (0.0577 g, 0.1 mmol), and  $\text{P}(\text{OCH}_2)_3\text{CEt}$  (0.0331 g, 0.204 mmol) was stirred at r.t. under argon. After 5 min, the dark violet solution turned yellow. Addition of **1** (0.0429 g, 0.109 mmol) to the mixture turned to clear yellow-green. The mixture was then stirred at  $80^\circ\text{C}$  under argon. After 40 h, no color change was observed and the GLC analysis of the resulting mixture showed that no **1** was consumed. In addition, the NMR analysis of the concentrate of the mixture showed the sample to be a simple mixture of  $\text{Pd}(\text{dba})_2$ , **L**, and **1**.

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