

## Organomagnesium Synthesis of *sec*-Butyl- and *tert*-Alkylchlorogermanes and Their Reaction with Ethynylmagnesium Bromide

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**Abstract**—The limits of application of organomagnesium synthesis to the substitution of chlorine atoms in tetrachlorogermane with bulky alkyl groups are established. The reaction of tetrachlorogermane with 2-butylmagnesium chloride leads to the substitution of one, two, or three chlorine atoms, yielding the corresponding alkylchlorogermanes  $(\text{MeEtCH})_n\text{GeCl}_{4-n}$ . The reaction of  $\text{GeCl}_4$  with *tert*-alkylmagnesium halides leads to the substitution of only one chlorine atom, yielding *tert*-alkyltrichlorogermanes  $\text{RMe}_2\text{CGeCl}_3$  ( $\text{R} = \text{Me}, \text{Et}, \text{Bu}$ ). *tert*-Butyltrichlorogermane reacts with ethylmagnesium bromide to give ethyl(*tert*-butyl)dichlorogermane. Isopropyltrichlorogermane reacts with *tert*-butylmagnesium chloride to give isopropyl(*tert*-butyl)dichlorogermane. This shows that the organomagnesium synthesis does allow linking of two bulky substituents to the germanium atom. The reaction of *tert*-alkyltrichlorogermanes and 2-butyltrichlorogermane in THF with ethynylmagnesium bromide, in which the hydrocarbon group is the most sterically accessible, allows substitution of all the three chlorine atoms, yielding the corresponding alkyl(triethynyl)germanes. The latter compounds react with the Grignard reagent and trimethylchlorosilane to give the corresponding alkyl(trimethylsilylethynyl)germanes.

The maximum number of bulky secondary and tertiary alkyl radicals capable of binding with an atom of a Group IV element M ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ ) by the reaction of the corresponding alkylmagnesium halides with  $\text{MX}_4$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) is determined by the atomic volume of the element M and halide X and the steric constant of the substituent R, i.e., by its volume and degree of branching.

It was found previously that isopropylmagnesium chloride can substitute only two chlorine atoms in tetrachlorosilane with the formation of diisopropyldichlorosilane [1, 2]. The reaction of isopropylmagnesium bromide with  $\text{SiF}_4$  allowed preparation of triisopropylfluorosilane [3]. Tetraisopropylsilane was prepared in a low yield (24%) only by the reaction of triisopropylfluorosilane with isopropyllithium [4]. This fact shows that, under rigid conditions, the silicon atom can be bound with four  $\text{CHMe}_2$  groups. *tert*-Butyltrichlorosilane was prepared by the reaction of  $\text{Me}_3\text{CLi}$  with  $\text{SiCl}_4$  or  $\text{HSiCl}_3$  in pentane [5]. Later  $\text{Me}_3\text{CSiCl}_3$  was prepared by the reaction of  $\text{Me}_3\text{C}\cdot\text{MgBr}$  with  $\text{Cl}_3\text{SiSiCl}_3$  [6].  $(\text{Me}_3\text{C})_2\text{SiCl}_2$  was prepared by the reaction of tetrachlorosilane with *t*-BuLi [7]. Organometallic synthesis is unsuitable for

preparing  $(\text{Me}_3\text{C})_3\text{SiCl}$ . This compound was obtained only by the reaction of  $\text{ICl}$  with  $(\text{Me}_3\text{C})_3\text{SiH}$  [8].

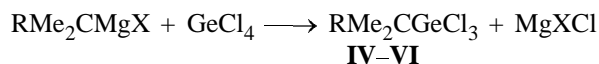
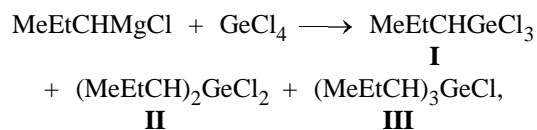
Among secondary alkyltrichlorogermanes, only 2-butyltrichlorogermane is known [9–11]. At the same time, *tert*-butylchlorogermanes of the general formula  $(\text{Me}_3\text{C})_n\text{GeCl}_{4-n}$  with  $n = 1–3$  were reported [7, 9–25].

Tetraisopropylgermane could not be prepared by the reaction of  $\text{GeBr}_4$  with excess isopropylmagnesium halide. In this case, only  $(\text{Me}_2\text{CH})_n\text{GeBr}_{4-n}$  with  $n = 1–3$  were isolated [26, 27]. All the attempts to prepare  $(\text{Me}_2\text{CH})_4\text{Ge}$  from  $\text{GeCl}_4$  led to the formation of triisopropylchlorogermane [26, 27]. Nevertheless, Carrick and Glockling [28] did obtain tetraisopropylgermane in 5–20% yield together with  $(\text{Me}_2\text{CH})_3\text{GeH}$  in the reaction of  $\text{GeCl}_4$  with excess  $\text{Me}_2\text{CHMgCl}$ .

Organomagnesium synthesis is hardly suitable for preparing sterically hindered alkylchlorostannanes  $\text{R}_{4-n}\text{SnCl}_n$  ( $n = 2, 3$ ;  $\text{R} = \text{Me}_2\text{CH}, \text{Me}_3\text{C}$ ). Tetra-*tert*-butyl- and tetra-*tert*-pentylstannanes could not be prepared by this method [29–31]. At the same time, four isopropyl radicals could be fairly readily linked to the tin atom by the Grignard reaction. The yield of  $(\text{Me}_2\text{CH})_4\text{Sn}$  reaches 60–85% [32–34].

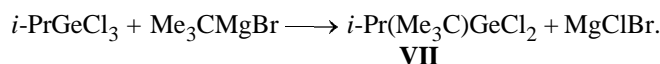
Alkylethynylgermanes  $R_{4-n}Ge(C\equiv CH)_n$  containing bulky alkyl groups are unknown up to now.

We have studied the reaction of tetrachlorogermane with 2-butyldimagnesium chloride and *tert*-alkylmagnesium halides. In the first case, we obtained the corresponding mono-, di-, and tri(2-butyl)-substituted  $(MeEtCH)_nGeCl_{4-n}$ ,  $n = 1$  (**I**), 2 (**II**), 3 (**III**), in 30–32% yields. In the reaction of  $GeCl_4$  with *tert*-alkylmagnesium chlorides or bromides  $RMe_2CMgX$  ( $R = Me, Et, Bu$ ;  $X = Cl, Br$ ), only one chlorine atom can be substituted. The corresponding *tert*-alkyltrichlorogermanes  $RMe_2CGeCl_3$  with  $R = Me$  (**IV**),  $Et$  (**V**),  $Bu$  (**VI**) were prepared in 76–96% yield.

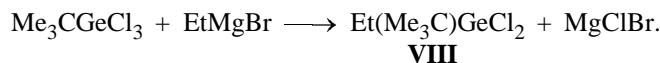


$R = Me$  (**IV**),  $Et$  (**V**),  $Bu$  (**VI**);  $X = Cl, Br$ .

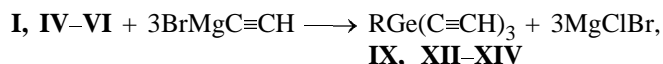
2-Butyltrichlorogermane does not react with *tert*-butylmagnesium bromide. This means that two sterically hindered radicals cannot be linked to the atom of germanium under the examined reaction conditions. At the same time, isopropyltrichlorogermane under the similar conditions gives isopropyl(*tert*-butyl)dichlorogermane **VII** in 72% yield.



The reaction of *tert*-butyltrichlorogermane with ethylmagnesium bromide gives ethyl(*tert*-butyl)dichlorogermane **VIII** in 70% yield.



*tert*-Alkyltrichlorogermanes **IV–VI** and 2-butyldichlorogermane **I** react in THF with ethynylmagnesium bromide containing the sterically accessible ethynyl group with the substitution of all the three chlorine atoms, yielding the corresponding alkyl(triethynyl)germanes **IX** and **XII–XIV**.



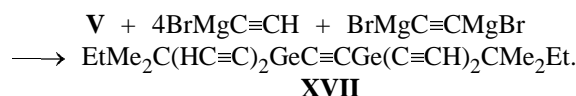
$R = MeEtCH$  (**IX**),  $Me_3C$  (**XII**),  $EtMe_2C$  (**XIII**),  $Me_2BuC$  (**XIV**).

Similarly, the reaction of ethynylmagnesium bromide

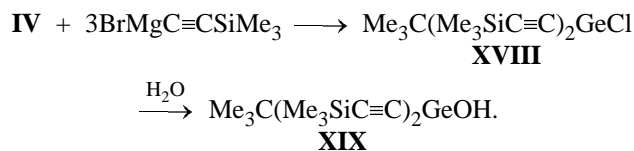
with ethyl(*tert*-butyl)-, isopropyl(*tert*-butyl)- and di-2-butyldichlorogermanes **II**, **VII**, and **VIII** allows substitution of both chlorine atoms by the ethynyl group, with the formation of dialkyl(diethynyl)germanes **X**, **XV**, and **XVI**.

And finally, sterically overcrowded tri(2-butyl)-chlorogermane **III** reacts with ethynylmagnesium bromide to form tri-2-butyl(ethynyl)germane **XI**.

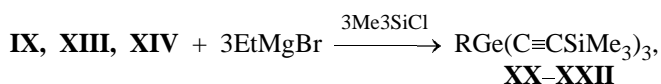
The reaction of *tert*-pentyltrichlorogermane **V** with ethynylmagnesium bromide and bis(bromomagnesium)acetylene in 2:4:1 molar ratio in THF gives highly unsaturated bis[*tert*-pentyl(diethynyl)germyl]acetylene **XVII**.



The reaction of *tert*-butyltrichlorogermane **IV** with trimethylsilylethynylmagnesium bromide in 1:3 molar ratio allows substitution of only two chlorine atoms with the formation of *tert*-butylbis(trimethylsilylethynyl)chlorogermane **XVIII**. Its hydrolysis gives the corresponding triorganylgermanol **XIX**.



Trimethylsilyl-substituted ethynylgermanes **XX–XXII** were prepared by the reaction of alkyl(triethynyl)germanes **IX**, **XIII**, and **XIV** containing a bulky alkyl group with ethylmagnesium bromide and trimethylchlorosilane in THF.



$R = MeEtCH$  (**XX**),  $Me_2EtC$  (**XXI**),  $Me_2BuC$  (**XXII**).

The yields and boiling points of the alkylchlorogermanes prepared are listed in Table 1, and those of alkylethynylgermanes, in Table 2. The structures of all the ethynyl compounds prepared were confirmed by  $^1H$ ,  $^{13}C$ , and  $^{29}Si$  NMR spectroscopy (Table 3).

## EXPERIMENTAL

The NMR spectra were obtained on a Bruker DRX-400 spectrometer (400 MHz) from 15% solutions in  $CDCl_3$  against internal HMDS.

**Table 1.** Yields, constants, and elemental analyses of chlorogermanes **I–VIII**

Comp. no.	Yield, %	bp, °C ( <i>p</i> , mm Hg)	$d_4^{20}$	$n_D^{20}$	Formula
<b>I</b>	30	61 (10)	1.4488	1.4735	C <sub>4</sub> H <sub>9</sub> Cl <sub>3</sub> Ge
<b>II</b>	31	82 (10)	1.2665	1.4715	C <sub>8</sub> H <sub>18</sub> Cl <sub>2</sub> Ge
<b>III</b>	32	93 (3)	1.1242	1.4755	C <sub>12</sub> H <sub>27</sub> ClGe
<b>IV<sup>a</sup></b>	96	70 (10)	–	–	C <sub>4</sub> H <sub>9</sub> Cl <sub>3</sub> Ge
<b>V<sup>b</sup></b>	90	75 (10)	–	–	C <sub>5</sub> H <sub>11</sub> Cl <sub>3</sub> Ge
<b>VI</b>	76	85 (1)	1.2073	1.4720	C <sub>7</sub> H <sub>15</sub> Cl <sub>3</sub> Ge
<b>VII</b>	72	65 (12)	1.2335	1.4762	C <sub>7</sub> H <sub>16</sub> Cl <sub>2</sub> Ge
<b>VIII</b>	70	83 (14)	1.2546	1.4720	C <sub>6</sub> H <sub>14</sub> Cl <sub>2</sub> Ge

<sup>a</sup> mp 104°C. Found, %: C 20.17; H 3.91; Cl 45.57; Ge 28.10. Calculated, %: C 20.34; H 3.84; Cl 45.06; Ge 30.75.

<sup>b</sup> mp 46°C.

Compounds **IX–XII** and **XIV–XVI** were prepared similarly.

**tert-Butylbis(trimethylsilylethynyl)chlorogermane XVIII** was prepared similarly from 11.75 g of **IV** and bromomagnesiethynyltrimethylsilane prepared from 3.62 g of Mg, 16.5 g of ethyl bromide, and 14.7 g of Me<sub>3</sub>SiC≡CH in 100 ml of THF. Vacuum sublimation gave 17.1 g (95%) of **XVIII**.

**2-Butyltrichloro-, di(2-butyl)dichloro-, and tri-(2-butyl)chlorogermanes I–III.** To a solution of 21.5 g of GeCl<sub>4</sub> in 50 ml of ether, 2-butybmagnesium chloride prepared from 4.86 g of magnesium, 18.5 g of *sec*-butyl chloride, and 100 ml of ether was added dropwise with stirring. After heating for 30 min, the reaction mixture was treated with water and 5% HCl. After the standard work-up and drying over calcined CaCl<sub>2</sub>, the solvent was distilled off. Fractionation of the residue in a vacuum gave 4.7 g (20%) of **I**, 7.3 g (31%) of **II**, and 7.5 g (32%) of **III**.

Compounds **IV–VIII** were prepared similarly.

**tert-Pentyl(triethynyl)germane XIII and bis-[tert-pentyl(diethynyl)germyl]acetylene XVII.** To a solution of 12.5 g of **V** in 50 ml of ether, ethynylmagnesium bromide prepared from 3.65 g of magnesium, 16.5 g of ethyl bromide, and acetylene in 100 ml of THF was added dropwise with stirring. After stirring for 1 h, the mixture was treated with water and 5% HCl. After the standard work-up and drying over calcined CaCl<sub>2</sub>, the solvents were distilled off in a water-jet-pump vacuum. The residue was distilled in a vacuum to give 15.4 g (71%) of **XIII**, and the subsequent vacuum (1 mm) sublimation of the residue on a boiling water bath gave 2.4 g (11%) of **XVII**.

**Table 2.** Yields, constants, and elemental analyses of ethynylgermanes **IX–XVII** and trimethylsilylethynylgermanes **XVIII–XXII**

Comp. no.	Yield, %	bp, °C ( <i>p</i> , mm Hg)	mp, °C	$d_4^{20}$	$n_D^{20}$	Found, %			Formula	Calculated, %		
						C	H	Ge		C	H	Ge
<b>IX</b>	80	65 (4)	–	1.1173	1.4713	58.61	5.96	34.77	C <sub>10</sub> H <sub>12</sub> Ge	58.64	5.91	35.45
<b>X</b>	80	85 (4)	–	1.0933	1.4733	60.90	8.45	29.37	C <sub>12</sub> H <sub>20</sub> Ge	60.84	8.51	30.64
<b>XI</b>	84	105 (4)	–	0.9967	1.4753	62.61	10.28	26.99	C <sub>14</sub> H <sub>28</sub> Ge	62.61	10.49	26.82
<b>XII</b>	81	70 (15)	75	–	–	58.32	6.00	35.35	C <sub>10</sub> H <sub>12</sub> Ge	58.64	5.91	34.45
<b>XIII</b>	71	70 (10)	75	–	–	60.25	6.92	32.21	C <sub>11</sub> H <sub>14</sub> Ge	60.38	6.45	33.17
<b>XIV</b>	80	85 (1)	–	1.0305	1.4610	–	–	–	C <sub>13</sub> H <sub>18</sub> Ge	63.24	7.35	29.40
<b>XV</b>	83	63 (12)	–	1.0439	1.4565	56.59	8.32	34.40	C <sub>10</sub> H <sub>16</sub> Ge	57.51	7.72	34.76
<b>XVI</b>	88	55 (1)	–	1.0450	1.4620	59.09	8.55	32.34	C <sub>11</sub> H <sub>18</sub> Ge	59.28	8.14	32.57
<b>XVII</b>	11	100 (1)	126	–	–	58.37	6.29	35.39	C <sub>20</sub> H <sub>26</sub> Ge <sub>2</sub>	58.36	6.37	35.27
<b>XVIII<sup>a</sup></b>	95	100 (1)	71	–	–	46.28	7.64	20.50	C <sub>14</sub> H <sub>27</sub> ClGeSi <sub>2</sub>	46.76	7.56	20.18
<b>XIX<sup>b</sup></b>	98	100 (1)	55	–	–	50.01	8.15	21.24	C <sub>14</sub> H <sub>28</sub> GeOSi <sub>2</sub>	49.28	8.27	21.28
<b>XX<sup>c</sup></b>	65	100 (1)	55	–	–	53.68	8.32	17.77	C <sub>19</sub> H <sub>36</sub> GeSi <sub>3</sub>	54.16	8.61	17.23
<b>XXI<sup>d</sup></b>	92	100 (1)	94	–	–	54.10	8.69	16.29	C <sub>20</sub> H <sub>38</sub> GeSi <sub>3</sub>	55.18	8.80	16.67
<b>XXII<sup>e</sup></b>	91	100 (1)	68	–	–	57.53	8.99	15.10	C <sub>22</sub> H <sub>42</sub> GeSi <sub>3</sub>	57.02	9.14	15.66

<sup>a</sup> Found, %: Cl 10.29; Si 15.39. Calculated, %: Cl 10.44; Si 15.62. <sup>b</sup> Found, %: Si 16.62. Calculated, %: Si 16.46. <sup>c</sup> Found, %: Si 20.86. Calculated, %: Si 20.00. <sup>d</sup> Found, %: Si 19.31. Calculated, %: Si 19.35. <sup>e</sup> Found, %: Si 17.73. Calculated, %: Si 18.18.

**Table 3.** Parameters of the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra of the compounds obtained

Comp. no.	$^1\text{H}$ NMR spectrum, $\delta$ , ppm		$^{13}\text{C}$ NMR spectrum, $\delta_{\text{C}}$ , ppm		
	RGe	HC $\equiv$	RGe	HC $\equiv$	GeC $\equiv$
<b>IX</b>	1.03 s ( <i>MeCH</i> <sub>2</sub> C), 1.22 s ( <i>MeC</i> ), 1.46 m (CH <sub>2</sub> ), 1.74 m (CH <sub>2</sub> )	2.45	12.92 (Me), 13.01 (Me), 24.85 (CH <sub>2</sub> ), 26.12 (CH)	93.99	80.27
<b>X</b>	1.01 s ( <i>MeCH</i> <sub>2</sub> C), 1.19 s ( <i>MeC</i> ), 1.47 m (CH <sub>2</sub> ), 1.74 m (CH <sub>2</sub> )	2.34	12.97 (Me), 15.26 (Me), 24.15 (CH <sub>2</sub> ), 26.20 (CH)	94.52	83.69
<b>XI</b>	0.98 s ( <i>MeCH</i> <sub>2</sub> ), 1.15 s ( <i>MeC</i> ), 1.38 m (CH <sub>2</sub> ), 1.70 m (CH)	2.24	13.52 (Me), 15.81 (Me), 22.56 (CH <sub>2</sub> ), 26.70 (CH)	94.18	87.72
<b>XII</b>	1.18 s	2.41	25.29 ( <i>Me</i> <sub>3</sub> C), 25.68 ( <i>Me</i> <sub>3</sub> C)	94.33	80.44
<b>XIII</b>	1.17 s ( <i>Me</i> ), 1.60 m (CH <sub>2</sub> )	2.45	24.22 ( <i>Me</i> <sub>2</sub> EtC), 33.36 ( <i>MeC</i> )	95.31	82.18
<b>XIV</b>	0.75 s ( <i>MeC</i> ), 1.17 s ( <i>MeC</i> <sub>4</sub> ), 0.91 m (CH <sub>2</sub> ), 1.19 m (CH <sub>2</sub> ), 1.26 m (CH <sub>2</sub> ), 1.50 m (CH <sub>2</sub> )	2.42	13.75 ( <i>MeBu</i> ), 23.25 ( <i>MeC</i> ), 27.00 (CH <sub>2</sub> ), 29.01 (CH <sub>2</sub> ), 36.00 (CH <sub>2</sub> ), 39.14 (CH <sub>2</sub> )	94.18	80.70
<b>XV</b>	1.04 s ( <i>MeCH</i> <sub>2</sub> ), 1.12 m (CH <sub>2</sub> ), 1.21 s ( <i>MeC</i> )	2.33	26.59 ( <i>Me</i> <sub>3</sub> C), 27.54 ( <i>Me</i> <sub>3</sub> C), 8.71 ( <i>MeCH</i> <sub>2</sub> ), 5.81 ( <i>MeCH</i> <sub>2</sub> )	93.99	83.01
<b>XVI</b>	1.18 s ( <i>MeCH</i> ), 1.20 s ( <i>MeC</i> ), 1.30 s ( <i>MeCH</i> )	2.35	25.48 ( <i>Me</i> <sub>3</sub> C), 27.28 ( <i>Me</i> <sub>3</sub> C), 19.49 ( <i>MeCH</i> <sub>2</sub> ), 17.75 ( <i>MeCH</i> <sub>2</sub> )	94.19	84.12
<b>XVII</b> <sup>a</sup>	1.17 s (Me), 1.60 m (CH <sub>2</sub> )	2.42	23.04 ( <i>Me</i> <sub>2</sub> EtC), 32.22 ( <i>MeC</i> )	94.41	80.93
<b>XVIII</b> <sup>b</sup>	1.21 s ( <i>MeC</i> )	—	25.06 ( <i>Me</i> <sub>3</sub> C), 29.36 ( <i>Me</i> <sub>3</sub> C)	—	—
<b>XIX</b> <sup>c</sup>	1.18 s ( <i>MeC</i> )	—	25.04 ( <i>Me</i> <sub>3</sub> C), 29.37 ( <i>Me</i> <sub>3</sub> C)	—	—
<b>XX</b> <sup>d</sup>	1.02 s ( <i>MeCH</i> <sub>2</sub> ), 1.17 s ( <i>MeCH</i> ), 1.36 m (CH <sub>2</sub> ), 1.70 m (CH)	—	12.92 (Me), 14.62 (Me), 25.52 (CH <sub>2</sub> ), 27.04 (CH)	—	—
<b>XXI</b> <sup>e</sup>	0.96 s ( <i>MeCH</i> <sub>2</sub> ), 1.11 s ( <i>MeC</i> ), 1.55 m (CH <sub>2</sub> )	—	9.13 ( <i>MeCH</i> <sub>2</sub> C), 23.02 ( <i>MeC</i> ), 29.54 ( <i>Me</i> <sub>2</sub> EtC), 32.14 (CH <sub>2</sub> )	—	—
<b>XXII</b> <sup>f</sup>	0.77 s ( <i>MeC</i> ), 0.91 m (CH <sub>2</sub> ), 1.13 s ( <i>MeC</i> <sub>4</sub> ), 1.20 m (CH <sub>2</sub> ), 1.30 m (CH <sub>2</sub> ), 1.48 m (CH <sub>2</sub> )	—	14.05 ( <i>MeBu</i> ), 23.85 ( <i>MeC</i> ), 27.20 (CH <sub>2</sub> ), 29.33 (CH <sub>2</sub> ), 36.08 (CH <sub>2</sub> ), 39.89 (CH <sub>2</sub> )	—	—

<sup>a</sup>  $^{13}\text{C}$  NMR spectrum:  $\delta_{\text{C}}$  104.99 ppm (GeC $\equiv$ ). <sup>b</sup>  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.23 s (CH<sub>3</sub>Si).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 102.56 (GeC $\equiv$ ), 116.89 ( $\equiv\text{CSi}$ ), -0.49 (CH<sub>3</sub>Si).  $^{29}\text{Si}$  NMR spectrum,  $\delta_{\text{Si}}$ , ppm: -16.95. <sup>c</sup>  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.20 s (CH<sub>3</sub>Si).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 102.55 (GeC $\equiv$ ), 116.90 ( $\equiv\text{CSi}$ ), -0.46 (CH<sub>3</sub>Si).  $^{29}\text{Si}$  NMR spectrum,  $\delta_{\text{Si}}$ , ppm: -16.95. <sup>d</sup>  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.23 s (CH<sub>3</sub>Si).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 104.09 (GeC $\equiv$ ), 114.75 ( $\equiv\text{CSi}$ ), -0.48 (CH<sub>3</sub>Si).  $^{29}\text{Si}$  NMR spectrum,  $\delta_{\text{Si}}$ , ppm: -17.06. <sup>e</sup>  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.16 s (CH<sub>3</sub>Si).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 104.13 (GeC $\equiv$ ), 114.90 ( $\equiv\text{CSi}$ ), -0.32 (CH<sub>3</sub>Si).  $^{29}\text{Si}$  NMR spectrum,  $\delta_{\text{Si}}$ , ppm: -18.05. <sup>f</sup>  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.18 s (CH<sub>3</sub>Si).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 104.23 (GeC $\equiv$ ), 114.94 ( $\equiv\text{CSi}$ ), -0.28 (CH<sub>3</sub>Si).  $^{29}\text{Si}$  NMR spectrum,  $\delta_{\text{Si}}$ , ppm: -18.32.

***tert*-Butylbis(trimethylsilylethynyl)germanol XIX.** Compound **XVII**, 14.4 g, was shaken in a funnel with 50 ml of ether and 15 ml of water. After the extraction and drying over calcined MgSO<sub>4</sub>, the solvent was distilled off, and the residue was sublimed in a vacuum to give 13.5 g (98%) of **XIX**.

***tert*-Pentyltris(trimethylsilylethynyl)germane XXI.** To a solution of *tert*-pentyltris(bromomagnesioethynyl)germane prepared from 1.44 g of magnesium, 6.6 g of ethyl bromide, and 4.36 g of **XIII** in 50 ml of THF, 6.48 g of Me<sub>3</sub>SiCl was added dropwise with stirring. After the decomposition of the reaction mixture, its standard work-up, and drying over calcined CaCl<sub>2</sub>, the solvent was removed, and the vacuum sublimation of the residue gave 8 g (92%) of **XXI**.

Compounds **XX** and **XXII** were prepared similarly.

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