A new catalytic route to synthesis of silylgermylethynes

Bogdan Marciniec *, Hanna Ławicka, Beata Dudziec

Adam Mickiewicz University, Faculty of Chemistry, Department of Organometallic Chemistry, Grunwaldzka 6, 60-780 Poznan, Poland

Abstract

Silylgermylethynes known to be potential organometallic reagents and precursors of optoelectronic materials can be efficiently synthesized via a recently reported catalytic method called silylative coupling of alkynes with vinylsilicon compounds. The reaction of triethylethynylgermane with vinyltrisubstituted silanes catalyzed by $[RuHCl(CO)(PR_3)_n]$ (where R = ^{i}Pr, Cy, Ph; n = 2–3) under optimal conditions selectively yields respective silylgermylethynes. Silylation of ethynylgermane with divinylsilicon derivatives such as siloxanes, silazanes, bis(silyl)benzene and bis(silyl)ethane gives monoethynylgermyl substituted vinyldisilicon products with high yields and selectivity, however, accompanied by traces of dialkynylgermyl derivatives. All catalytic results as well as those of stoichiometric study on the insertion of ethynylgermane into Ru–Si bond have permitted proposing mechanistic schemes of the reaction examined.
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1. Introduction

Functionalized alkynylsilanes and alkynylgermanes are used separately as alkynylation agents in synthesis of organic, organometallic and natural products [1]. Moreover, both silicon and germanium compounds possessing π-conjugated systems have been considered (also as combined silicon germanium derivatives) as potential precursors of optoelectronic materials, particularly candidates for electronic devices [2]. Alkynyl derivatives of silicon and germanium can be prepared by various methodologies involving classical stoichiometric routes from organometallic reagents [3] as well as more recently (particularly alkynylsilanes) by metal-catalyzed silylation of terminal alkynes [4].

In the last two decades we have developed a new type of transition metal-catalyzed reaction of vinylsubstituted organoelement (E) (where E = Si, Ge, B) compounds with olefins called silylative (for review see [5]), germylative [6] and borylative [7] coupling that is complementary to olefin metathesis (for comparison of these reactions see [5] and [11]) and proceeds according to the following general Eq. (1):
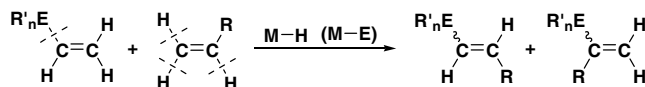

where   E = Si, B, Ge   M = Ru, Rh, Ir

R = Ph, OR'', NR_2, OCOR''   R' = alkyl, aryl, alkoxyl

(1)

The reaction occurs by activation of sp^2 carbon–hydrogen bond and sp^2 carbon–heteroatom (E) bond. Very recently we have reported on the activation of sp-hybridized carbon–hydrogen bonds by such vinyl metalloids (particularly by vinylsilicon [8] and vinylgermanium [9] derivatives). The reaction (see Eq. (2)), called the cross-coupling of alkynes with vinylsilicon and vinylgermanium compounds, proceeds in the presence of complexes containing [Ru]–H and/or [Ru]–Si bonds. Only in some cases the target silylethynes and germylethynes have been accompanied by products of homo-coupling of vinylmetaloid compounds used in excess.

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* Corresponding author. Tel.: +48 0618291366; fax: +48 0618291508.
 E-mail address: bogdan.marciniec@amu.edu.pl (B. Marciniec).

where E = Ge, Si

(by-product)

**product of
homo-coupling of vinylmetaloid**

(2)
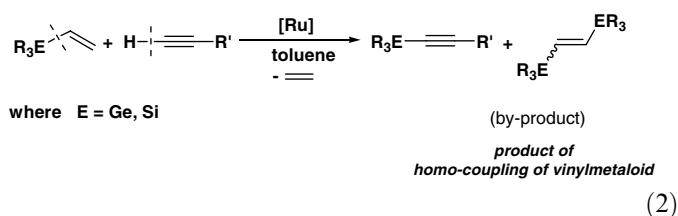
The aim of the study reported here is to show the possibility of application of the new catalytic route involving coupling of ethynylgermane with vinylsilicon compounds for selective synthesis of silylgermylethynes, otherwise difficult to achieve using alternative synthetic routes.

2. Results and discussion

Similarly to the previous reports [8a,9] [RuHCl(CO)(PCy$_3$)$_2$] and [RuHCl(CO)(PPh$_3$)$_3$] appeared to be the most effective catalysts in the following reaction (see Eq. (3)):
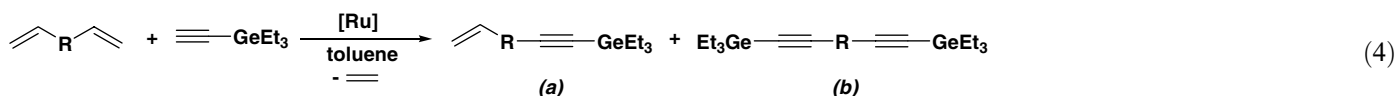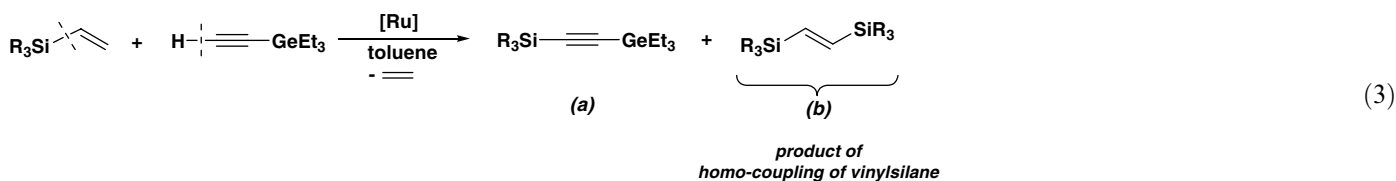
The reaction was successfully performed under argon atmosphere (open glass ampoules) in 100 °C, its products were detected by GC and GC–MS methods and identified by ^{1}H and ^{13}C NMR spectroscopy. Triethylethynylgermane was used as a substrate in this reaction (Table 1). Silylation of ethynylgermane derivatives required more catalyst (2%) rather than the used in silylation (1%), however reducing the amount of catalyst affects only the time of the reaction (48 not 24 h), not the selectivity [9].

As we have found [8a] the equimolar reaction of vinylsilanes with alkynes gives some enynes as products of alkyne dimerization. For exclusion of enynes, vinylsilanes must be used in excess. On the other hand, a twofold excess of vinylsilane yields silylgermylethynes but accompanied by a product of vinylsilane homo-coupling. The reaction conditions needed to be optimized for the exclusive formation of the product desired and the 1.5-fold excess of vinylsilicon compounds was the best amount to be employed.

Silylation of ethynylgermane by divinylsubstituted silicon compounds at a twofold excess of vinylsilicon substrate gives monoethynylgermyl substituted vinyldisilicon products with high yields and selectivity (see Eq.

(4)). However, in all cases the main products were accompanied by traces of dialkynylgermyl derivatives (Table 2). There should be emphasized that, in view of the known synthetic procedures, monoethynylgermyl substituted vinyldisilicon products, especially with both acetylene and vinyl functionalities are difficult to be synthesized by other methods. This fact may be crucial to admit the great importance of the silylation of ethynylgermane with divinylsilicon derivatives reported here.

The results of catalytic experiments on silylation of ethynylgermane and previously reported stoichiometric study of insertion of acetylenes into Ru–Si bond [8–10] allow us to propose the following mechanistic scheme of the reaction studied (Scheme 1):

The reaction scheme involves an insertion of ethynylgermane into the [Ru]–Si bond (via route proposed earlier, regarding the way of *cis–trans* isomerisation; see [11]) followed by elimination of silylethynylgermane product (for mechanistic consideration see [10]). The consecutive

(a)

(b)

**product of
homo-coupling of vinylsilane**

(3)

(a)

(b)

(4)

Table 1
Catalytic transformation of triethylethynylgermane via *cross*-coupling with vinylsilanes

SiR$_3$	Conversion of Et$_3$GeC≡CH (%)	Selectivity (%) a/b (refers to the compounds **a** and b) **a** – major product
SiMe$_2$Ph	87	**100**
	52[a]	**97/3**
	41[b]	**100**
	90[c]	**92/2**
	75[d]	**93/5**
Si(OEt)$_3$	76	**99/1**
SiMe(OSiMe$_3$)$_2$	32	**100**
	61[c]	**98/2**
SiMe$_2$(OSiMe$_3$)	57	**100**
	99[c]	**96/4**

Reaction conditions: Ar, open glass ampoules, toluene (0.5 M), $t = 24$ h, $T = 100$ °C.
[Ru] = [RuHCl(CO)(PCy$_3$)$_2$], [Ge] = [Et$_3$GeC≡CH], [Si] = [R$_3$SiCHCH$_2$].
[Ru]:[Ge]:[Si] = 2×10^{-2}:1:1.5.
[a] [Ru]:[Ge]:[Si] = 10^{-2}:1:2.
[b] [RuHCl(CO)(PPh$_3$)$_3$]:[Ge]:[Si] = 2×10^{-2}:1:1.5.
[c] [Ru]:[Ge]:[Si] = 2×10^{-2}:1:2.
[d] [Ru(SiMe$_3$)Cl(CO)(PCy$_3$)$_2$]:[Ge]:[Si] = 2×10^{-2}:1:1.5.
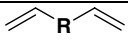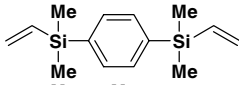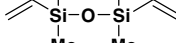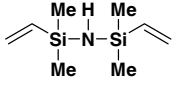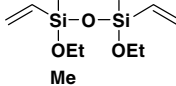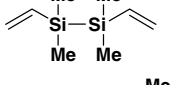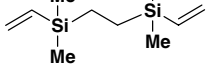
Table 2
Catalytic transformation of triethylethynylgermane via *cross*-coupling with divinylsilicon derivatives catalyzed by [RuHCl(CO)(PCy$_3$)$_2$]

No.	⟍⟋R⟍⟋	Conversion of Et$_3$GeC≡CH (%)	Selectivity (%) a/b (refers to the compounds **a** and b) **a** – major product
1	Me Me / Si—C$_6$H$_4$—Si / Me Me (p-phenylene bis(dimethylsilyl) divinyl)	99	**90**/10
2	Me Me / Si—O—Si / Me Me	68	**95**/5
3	Me H Me / Si—N—Si / Me Me	74	**95**/5
4	OEt OEt / Si—O—Si / OEt OEt	70	**94**/6
5	Me / Si / Me	0[a]	
6	Me Me / Si—Si / Me Me	12	Mixture of unidentified products
7	Me Me / Si—CH$_2$CH$_2$—Si / Me Me	86	**97**/3

Reaction conditions: open system, toluene (0.5 M), *t* = 24 h, 110 °C. [RuHCl(CO)(PCy$_3$)$_2$]:[Et$_3$GeC≡CH]:[(CH$_2$=CH)$_2$R] = 2 × 10^{-2}:1:2.
[a] Closed system.

insertion of vinylsilicon compounds into the [Ru]–H bond followed by β-Si-elimination of ethylene is well-documented [7].

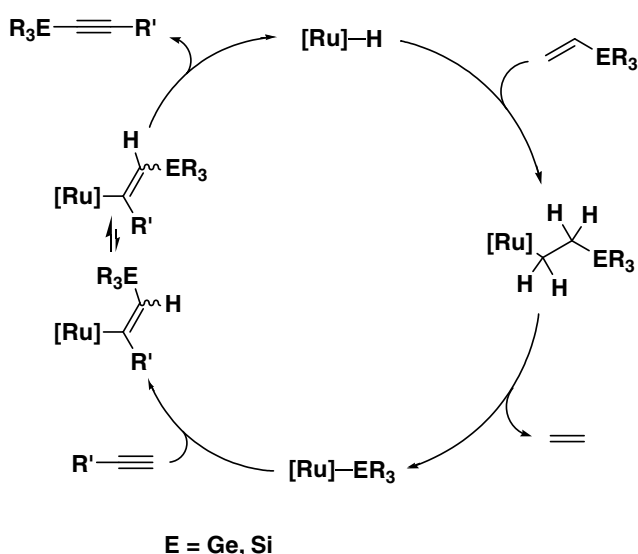Although this general mechanism had been proved by the stoichiometric study reported earlier [8a] we performed

E = Ge, Si

Scheme 1. Mechanism of coupling of triethylethynylgermane with vinyl-substituted silicon compounds.

the reaction of equimolar amounts of [Ru(SiMe$_3$)Cl(CO)(PPh$_3$)$_2$] with triethylethynylgermane which occurs as follows (Scheme 2): (identified by ^{1}H NMR spectroscopy and GC–MS).

The spectra allowed a detection of formation of the [Ru]–H complex (confirmed by the appearance of a doublet of triplets at −6.63 ppm (J_{H-P} = 105.2 Hz, J_{H-P} = 24.3 Hz)) – a product of acetylene insertion into [Ru]–Si complex, followed by the elimination of the substituted ethyne compound (see Fig. 1a). There is a visible decrease in the amount of [Ru]–H moiety as temperature rises. The created *in situ* [Ru]–H complex and triethylethynylgermane (present in the system in slight excess – see Section 4) reacted towards ruthenium–vinylene complex and this progress of the reaction was also controlled by NMR analysis. The amount of the vinylene complex increased with increasing temperature (see Fig. 1b). In the absence of vinylgermane [8a,10], the [Ru]–H complex is active in the hydrogenation of acetylenes (see the ratios of compounds after the completion of the equimolar reaction (Scheme 2).

3. Conclusion

In conclusion, we have shown that the new general reaction of silylative coupling of acetylenes catalyzed by [RuHCl(CO)(PCy$_3$)$_2$] or [RuHCl(CO)(PPh$_3$)$_3$], reported here, can be a valuable tool for selective synthesis of silylethynylgermanes and vinylsilylgermylalkynyl derivatives of both, acetylene and vinyl functionalities. These compounds may play a very important role as potent organometallic reagents and precursors of e.g. optoelectronic materials.

4. Experimental

4.1. General methods

^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz) and DEPT spectra were recorded on a Varian XL 300 MHz spectrometer in CDCl$_3$ (or C$_6$D$_5$CD$_3$) solution. Chemical shifts are reported in δ (ppm) with reference to the residue portion solvent (CHCl$_3$) peak assigned to ^{1}H and ^{13}C NMR. Gas chromatographic (GC) analyses were performed on a Varian 3300 with a DB-5 fused silica capillary column (30 m × 0.15 mm) and TCD. Mass spectra of the monomers and products were obtained by GC–MS analysis (Varian Saturn 2100 T, equipped with a BD-5 capillary column (30 m) and an ion trap detector). Thin-layer chromatography (TLC) was made on plates coated with 250 μm thick silica gel (Aldrich and Merck), and column chromatography was conducted with Silica Gel 60 (70–230 mesh, Fluka).

4.2. Materials

The chemicals were obtained from the following sources: toluene, dodecane, pentane and hexane, were

Scheme 2. The reaction of equimolar amounts of [Ru(SiMe₃)Cl(CO)(PPh₃)₂] with triethylethynylgermane.

Fig. 1. Temperature dependence of the ¹H NMR spectra of the reaction of [Ru(SiMe₃)Cl(CO)(PPh₃)₂] with triethylethynylgermane.

purchased from Fluka, CDCl₃, C₆D₅CD₃ from Dr. Glaser A.G. Basel. The substituted acetylenes were bought from Aldrich. The HC≡CGeEt₃ were prepared according to the literature procedure [9]. The ruthenium complexes [RuHCl(CO)(PCy₃)₂], [RuHCl(CO)(PPh₃)₃], [Ru(SiMe₃)-Cl(CO)(PPh₃)₂] were prepared according to the literature procedure [12]. Toluene and pentane were dried by distillation from sodium hydride, similarly hexane was distilled from calcium hydride under argon. All liquid substrates were also dried and degassed by bulb-to-bulb distillation. All the reactions were carried out under dry argon atmosphere.

4.3. Procedure for synthesis of [Ru(SiMe₃)Cl(CO)(PCy₃)₂]

H₂C=CHSiMe₃ (0.243 mL, 1.7 mmol) was added via a syringe to the refluxing solution of [RuHCl(CO)(PCy₃)₂] (244 mg, 0.34 mmol) in benzene (10 mL) and the reaction mixture was refluxed for 72 h. The solvent was evaporated under reduced pressure and 15 mL of cold pentane

(−50 °C) was added. The supernatant was removed and the yellow precipitate was washed three times with pentane (at −50 °C) and dried in vacuo. Yield 85%.

Analytical data: ¹H NMR (C₆D₆; δ (ppm)): 0.31 (s, 9H, SiC*H*₃), 1.18–2.60 (m, 33H, P(C₆*H*₁₁)₃); ¹³C NMR (C₆D₆; δ (ppm)): 1.62 (Si*C*H₃), 26.75–35.28 (P(*C*₆H₁₁)₃), 202.10 (*C*O); ³¹P NMR (C₆D₆; δ (ppm)): 46.63 (*P*(C₆H₁₁)₃).

4.4. The reaction of equimolar amounts of [Ru(SiMe₃)Cl(CO)(PPh₃)₂] with triethylethynylgermane

In a test, the ruthenium catalyst [Ru(SiMe₃)Cl (CO)(PPh₃)₂] was dissolved in toluene-*d*₈ and placed in an NMR ampoule under argon. The ampoule was cooled in liquid nitrogen then triethylethynylgermane was added (at the molar ratio: [Ru]:[triethylethynylgermane] = 1:1.2). After that, the ampoule was inserted into a Brucker Ultra Shield spectrometer (600 MHz) and slowly heated. The spectra were recorded at different temperatures between −20 and +60 °C, changed at a step of 10 °C.

4.5. Representative procedure for synthesis of [Et₃Ge–C≡C–SiR₃]

In a typical test, the ruthenium catalyst [RuH(Cl)(CO)(PCy₃)₂] (2 mol%) was dissolved in toluene and placed in a glass ampoule under argon. Then the reagents and decane as internal standard (5% by volume all components), triethylethynylgermane and vinylsilane (usually used at the molar ratio: [Ru]:[Et₃GeC≡CH]:[R₃SiCH=CH₂] = 2×10^{-2}:1:1.5 or 2×10^{-2}:1:2) were added. After that, the ampoule was heated to 100 °C and maintained at that temperature for 24 h. The final products were separated from the residues of the catalyst and reactants by using a column with silica. The progress of the reaction was controlled by GC and GC–MS. All products of catalytic transformation of triethylethynylgermane and vinylsilane were oily liquids.

4.6. Representative procedure for synthesis of [H₂C=CH–R–C≡C–GeEt₃ and Et₃Ge–C≡C–R–C≡C–GeEt₃]

In a typical test, the ruthenium catalyst [RuH(Cl)(CO)(PCy₃)₂] (2 mol%) was dissolved in toluene and placed in a glass ampoule under argon. Then the reagents and decane as internal standard (5% by volume all components), triethylethynylgermane and divinylsilane (at the molar ratio: [Ru]:[Et₃GeC≡CH]:[(CH₂=CH)₂R] = 2×10^{-2}:1:2) were added. After that, the ampoule was heated to 110 °C and maintained at that temperature for 24 h. The final products were separated from the residues of the catalyst and reactants by using a column with silica. The progress of the reaction was controlled by GC and GC–MS. All products of catalytic transformation of triethylethynylgermane and divinylsilicon compound were oily liquids.

4.6.1. 1-Phenyldimethylsilyl-2-(triethylgermyl)ethyne

Analytical data: ¹H NMR (CDCl₃; δ (ppm)): 0.41 (s, 6H, SiCH₃), 0.86 (q, 6H, GeCH₂CH₃, J_{H-H} = 8.1 Hz), 0.92 (t, 9H, GeCH₂CH₃, J_{H-H} = 8.1 Hz), 7.36–7.69 (m, 5H, CH).
¹³C NMR (CDCl₃; δ (ppm)): −0.37 (SiCH₃), 5.85 (GeCH₂CH₃), 9.08 (GeCH₂CH₃), 111.58 (Ge–C≡C), 113.88 (Si–C≡C), 127.65 (CH), 129.11 (CH), 133.62 (CH), 137.37 (cᵢ-C₆H₅).
MS (EI) [m/z (%)] = 319 (M⁺, 3), 291 (M⁺·−CH₂CH₃, 100), 263 (65), 235 (22), 171 (3), 159 (12), 145 (13), 105 (8), 89 (4), 75 (8), 53 (4). Elemental Anal. Calc. for C₁₆H₂₆Ge: C, 60.22; H, 8.21. Found: C, 60.18; H, 8.22%. Isolated yield 80%.

4.6.2. 1-Triethoxysilyl-2-(triethylgermyl)ethyne

Analytical data: MS (EI) [m/z (%)] = 319 (M⁺·−CH₂CH₃, 22), 291 (100), 275 (11), 263 (34), 247 (39), 219 (20), 203 (15), 189 (9), 175 (10), 161 (12), 133 (10), 101 (7), 73 (5).

4.6.3. 1-Bis(trimethylsiloxy)methylsilyl-2-(triethylgermyl)-ethyne

Analytical data: ¹H NMR (CDCl₃; δ (ppm)): 0.14 (s, 18H, OSiCH₃), 0.16 (s, 3H, SiCH₃), 0.87 (q, 6H, GeCH₂CH₃, J_{H-H} = 8.1 Hz), 1.09 (t, 9H, GeCH₂CH₃, J_{H-H} = 8.1 Hz).
¹³C NMR (CDCl₃; δ (ppm)): 1.79 (OSiCH₃), 2.00 (SiCH₃), 5.68 (GeCH₂CH₃), 9.01 (GeCH₂CH₃), 108.78 (Ge–C≡C), 112.96 (Si–C≡C).
MS (EI) [m/z (%)] = 377 (M⁺·−CH₂CH₃, 20), 363 (33), 349 (100), 321 (25), 231 (6), 215 (17), 201 (8), 147 (25), 133 (31), 119 (29), 73 (33), 59 (4). Elemental Anal. Calc. for C₁₅H₃₆GeO₂Si₃: C. 44.45; H, 8.95; O, 7.87. Found: C, 44.41; H, 8.96; O, 7.84%. Isolated yield 55%.

4.6.4. 1-(Trimethylsiloxy)dimethylsilyl-2-(triethylgermyl)-ethyne

Analytical data: MS (EI) [m/z (%)] = 333 (M⁺·, 1), 289 (M⁺·−SiCH₃, 17), 275 (M⁺·−CH₂CH₃, 100), 247 (61), 171 (3), 157 (15), 143 (14), 103 (4), 89 (5), 73 (17), 59 (3).

4.6.5. 1-[(Triethylgermylethynyl)dimethylsilyl]-4-(dimethylvinylsilyl)benzene

Analytical data: ¹H NMR (CDCl₃; δ (ppm)): 0.35 (s, 6H, SiCH₃), 0.39 (s, 6H, SiCH₃), 0.89 (q, 6H, GeCH₂CH₃, J_{H-H} = 8.1 Hz), 1.11 (t, 9H, GeCH₂CH₃, J_{H-H} = 8.1 Hz), 5.76 (dd, 1H, Si–HC=CH₂), 6.06 (dd, 1H, Si–HC=CH₂), 6.29 (dd, 1H, Si–HC=CH₂), 7.56 (d, 2H, C₆H₄), 7.65 (d, 2H, C₆H₄).
¹³C NMR (CDCl₃; δ (ppm)): −2.88 (SiCH₃), −0.40 (SiCH₃), 5.85 (GeCH₂CH₃), 9.08 (GeCH₂CH₃), 111.42 (Ge–C≡C), 113.93 (Si–C≡C), 132.75 (Si–CH=CH₂), 132.92 (CH), 133.01 (CH), 137.76 (Si–CH=CH₂), 138.13 (cᵢ-C₆H₄), 139.37 (cᵢ-C₆H₄).
MS (EI) [m/z (%)] = 375(M⁺·−CH₂CH₃, 100), 347 (90), 319 (57), 291 (35), 271 (6), 257 (10), 215 (20), 187 (9), 161 (19), 145 (24), 131 (15), 105 (9), 73(24), 59 (32). Elemental Anal. Calc. for C₂₀H₃₄GeSi₂: C, 59.56; H, 8.50; O, 7.87. Found: C, 59.50; H, 8.48%. Isolated yield 92%.

4.6.6. 1-[(Triethylgermylethynyl)]-1,1,3,3-tetramethyl-3-vinyl-disiloxane

Analytical data: ¹H NMR (CDCl₃; δ (ppm)): 0.19 (s, 6H, SiCH₃), 0.22 (s, 6H, SiCH₃), 0.87 (q, 6H, GeCH₂CH₃, J_{H-H} = 8.1 Hz), 1.07 (t, 9H, GeCH₂CH₃, J_{H-H} = 8.1 Hz), 5.76 (dd, 1H, Si–HC=CH₂), 5.94 (dd, 1H, Si–HC=CH₂), 6.16 (dd, 1H, Si–HC=CH₂).
¹³C NMR (CDCl₃; δ (ppm)): 2.45 (SiCH₃), 2.61 (SiCH₃), 5.74 (GeCH₂CH₃), 9.02 (GeCH₂CH₃), 110.75 (Ge–C≡C), 113.49 (Si–C≡C), 131.61 (Si–CH=CH₂), 139.17 (Si–CH=CH₂).
MS (EI) [m/z (%)] = 343 (M⁺·, 1), 287 (M⁺·−2 · CH₂CH₃, 100), 259 (54), 231 (8), 197 (6), 183 (12), 169 (37), 143 (19), 117 (13), 103 (10), 73 (24), 59 (8). Elemental Anal. Calc. for C₁₄H₃₀GeOSi₂: C, 48.99; H, 8.81; O, 4.66. Found: C, 49.03; H, 8.84; O, 4.70%. Isolated yield 60%.

4.6.7. 1-[(Triethylgermylethynyl)dimethylsilyl]-2-(dimethylvinylsilyl)ethane

Analytical data: ^{1}H NMR (CDCl$_3$; δ (ppm)): 0.05 (s, 6H, SiCH$_3$), 0.07 (s, 6H, SiCH$_3$), 0.53 (m, 4H, CH$_2$–CH$_2$), 0.85 (q, 6H, GeCH$_2$CH$_3$, J_{H-H} = 8.1 Hz), 1.07 (t, 9H, GeCH$_2$CH$_3$, J_{H-H} = 8.1 Hz), 5.67 (dd, 1H, Si–HC=CH$_2$), 5.92 (dd, 1H, Si–HC=CH$_2$), 6.14 (dd, 1H, Si–HC=CH$_2$).

^{13}C NMR (CDCl$_3$; δ (ppm)): −3.96 (SiCH$_3$), −2.11 (SiCH$_3$), 5.69 (GeCH$_2$CH$_3$), 7.39 (–CH$_2$–CH$_2$–), 8.55 (–CH$_2$–CH$_2$–), 8.95 (GeCH$_2$CH$_3$), 111.83 (Ge–C≡C), 113.39 (Si–C≡C), 131.52 (Si–CH=CH$_2$), 139.02 (Si–CH=CH$_2$).

MS (EI) [m/z (%)] = 326 (M^{+}·−CH$_2$CH$_3$, 17), 313 (10), 299 (67), 271 (50), 243 (15), 209 (15), 195 (100), 181 (20), 155 (22), 129 (18), 103 (12), 85 (31), 73 (16), 59 (86). Elemental Anal. Calc. (%) for C$_{16}$H$_{34}$GeSi$_2$: C, 54.09; H, 9.65. Found: C, 54.13; H, 9.62%. Isolated yield 82%.

4.6.8. 1-[(Triethylgermylethynyl)]-1,1,3,3-tetraethoxy-3-vinyl-disiloxane

Analytical data: MS (EI) [m/z (%)] = 465 (M^{+}·, 1), 351 (66), 291 (100), 259 (28), 247 (22), 215 (13), 199 (12), 159 (12), 129 (7), 101 (7), 73 (6).

4.6.9. 1-[(Triethylgermylethynyl)]-1,1,3,3-tetramethyl-3-vinyl-disilazane

Analytical data: MS (EI) [m/z (%)] = 465 (M^{+}·−CH$_2$CH$_3$, 18), 286 (100), 258 (70), 216 (11), 196 (11), 182 (44), 168 (44), 154 (19), 142 (35), 116 (16), 100 (24), 73 (23), 59 (11).

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