New Catalytic Route to Alkynylgermanes[†]

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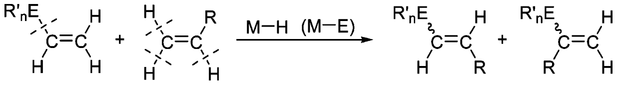
Vinyl-trisubstituted germanes react selectively with terminal alkynes in the presence of compounds containing Ru−H and Ru−Ge bonds with formation of functionalized alkynylgermanes. The reaction opens the first transition metal catalytic route for the preparation of this class of organogermanes, which are useful reagents for organic synthesis. The mechanism elucidated by NMR spectroscopic study of stoichiometric reactions shows that this process is a new catalytic activation of an sp-hybridized C−H bond involving the previously discovered activation of the ═C−Ge bond.

Introduction

Organogermanium compounds have recently been recognized as useful reagents for organic synthesis.[1,2] Unsaturated germanes are of very low toxicity and therefore can serve as alternatives to the organotin compounds.[3] Functionalized alkynylgermanes, in particular, have been useful synthons in cross-coupling reactions[4a−c] as well as in cycloaddition of azides[4d−g] and synthesis of other organometallic reagents[4h−j] and oligosaccharides.[4l,m] Germanium-based compounds possessing a π-conjugated system are also considered (along with the respective silicon compounds) to be potential candidates for electronic devices thanks to their photo- and electroluminescent properties.[5]

Alkynylgermanium compounds can be prepared by various methodologies involving classical stoichiometric organometallic routes that can be classified into three groups, i.e., the reactions of organogermanium halides with metal acetylides,[6] germylation of terminal alkynes,[7] and modification of preformed alkynylgermanes[8] (for a recent review see ref 9).

Scheme 1. Silylative, Borylative, and Germylative Coupling of Olefin with Vinyl-Substituted Organometallic Compounds



where E = Si, B, Ge; R' = alkyl, aryl, alkoxyl
M = Ru, Rh, Ir; R = Ph, OR", NR$_2$, OCOR"

In the last two decades we have developed a new type of transition metal (TM)-catalyzed reaction of vinyl-substituted organometallic (E) (where E = Si, Ge, B) compounds with olefins such as silylative (for review see ref 10), germylative,[11] and borylative[12] coupling that is complementary to metathesis and proceeds according to Scheme 1.

The reaction occurs by cleavage of the ═C−H bond in an olefin and the ═C−E bond in vinyl-substituted organometallic compounds.[10−13] Very recently we have reported a new catalytic reaction that also involves coupling of terminal alkynes with vinylsilicon compounds to form silylacetylenes. This reaction

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[†] Dedicated to Professor Florian Domka on the occasion of his 75th birthday.

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(1) For example: (a) Kawashima, T. *J. Organomet. Chem.* **2000**, *611*, 256−263. (b) Faller, J. W.; Kultyshev, R. G. *Organometallics* **2002**, *21*, 5911−5918. (c) Anod, W.; Itoh, H.; Tsumuraya, T. *Organometallics* **1989**, *8*, 2759−2766. (d) Curran, D. P.; Diederichsen, U.; Palovich, M. *J. Am. Chem. Soc.* **1997**, *119*, 4797−4804. (e) Piers, E.; Marais, P. C. *J. Org. Chem.* **1990**, *55*, 3454−3455.

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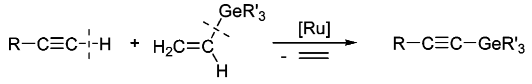
Scheme 2. Germylative Coupling of Terminal Alkynes with Vinyl-Substituted Germanes



R = alkyl, cycloalkyl, SiR''$_3$, GeR''$_3$, R'$_3$ = Et$_3$, PhMe$_2$

opens a new catalytic route for the activation of sp-hybridized C−H bonds.[14] Moreover, we have found that this mode of reactivity, which is well known for vinylsilicon compounds, seems to be more general and is also exhibited by vinylgermanes.[11] In this paper, therefore, we report a new catalytic transformation of vinyl-trisubstituted germanes of the general formula $CH_2{=}CHGeR_3$ (where GeR_3 is $GeEt_3$ and $GePhMe_2$) with selected alkynes, which by analogy can be called germylation (germylative coupling) of alkynes by vinylgermanes.[15]

Results and Discussion

The reaction of germylative coupling, which proceeds in the presence of complexes containing [Ru]−H and/or [Ru]−Ge bonds such as $[RuHCl(CO)(PCy_3)_2]$ (**I**), $[RuHCl(CO)(P\textit{i}\text{-}Pr_3)_2]$ (**II**), $[RuHCl(CO)(PPh_3)_3]$ (**III**), $[Ru(GeEt_3)Cl(CO)(PPh_3)_2]$ (**IV**), and $[RuH(CO)(MeCN)_2(PCy_3)_2]^+[BF_4]^-$ (**V**), leads (under optimum conditions) to the formation of germyl-substituted derivatives with evolution of ethylene (see Scheme 2).

To our knowledge it is the first direct TM-catalyzed process for the preparation of alkynyl germanes. The reaction was examined in an open system in toluene at 110 °C under a gentle stream of argon. Only for the volatile *tert*-butylacetylene was the process conducted in a closed system. Germylation of alkyne required a little more time than the silylation of alkynes and required more catalyst (2%) than used in silylation (1%) (Table 1).[14a] While alkyl, cycloalkyl, silyl, and germyl ethynes reacted efficiently in this process, the germylation of phenylacetylene (as had been formed in the reaction with vinylsilanes[14a]) did not occur.

Since the equimolar reaction of vinylgermanes with alkynes yielded some enyne byproducts as a result of the alkyne dimerization, a 2- to 3-fold excess of vinylgermane is necessary to prevent this reaction.

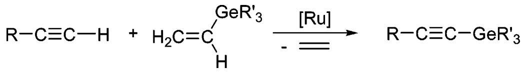
The turnover frequency parameters (TOF) were calculated for selected reactions and are comparable to those found for silylation (see Table 1). Reaction products were characterized by GC and GC-MS methods and identified by ^1H and ^{13}C NMR spectroscopy.

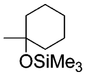
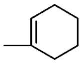
In order to provide evidence for the insertion of alkyne into the Ru−Ge bond, the $[Ru(GeEt_3)Cl(CO)(PPh_3)_2]$ (catalyst **IV**) equimolar reactions were carried out with some alkynes—ethynyltriethylsilane, ethynyltriethylgermane, and phenylacetylene—to yield the respective main insertion products (identified by GC-MS and ^1H NMR spectroscopy) and ruthenium complexes formed according to Scheme 3.

The NMR spectra were measured at various temperatures during the reactions, between −20 and +60 °C (at 10 °C intervals of temperature) and showed significant differences in the reaction of **IV** with the substituted acetylenes studied. The reaction with phenylacetylene occurs in the same manner as that previously found in the case of the [Ru]−Si complex,[14a] i.e., forming immediately even at −20 °C vinylenephenyleneruthenium complex **VI** $[Ru(Cl)(CO)(PPh_3)_2(CH{=}CHPh)]$, and no [Ru]−H was detected. The characteristic feature of this reaction followed by GC-MS analysis is an almost quantitative conversion of phenylacetylene, leading to a high excess of the primary product (Et_3GeCCH) over secondary products of phenylacetylene hydrogenation (styrene) and dimerization (enyne) (see the ratio of products in brackets in Scheme 3, path (1)). The respective spectrum is identical to those presented in our previous communication.[14a] The corresponding reactions of **IV** with ethynyltriethylsilane and ethynyltriethylgermane at low temperatures allowed the detection of a [Ru]−H complex, as 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). They compose vinylenesilylene and vinylenegermyleneruthenium analogues **VII** $[RuCl(CO)(PPh_3)_2(CH{=}CHSiEt_3)]$ and vinylenegermyleneruthenium **VIII** $[RuCl(CO)(PPh_3)_2(CH{=}CHGeEt_3)]$ at room temperature, respectively (see Figures 1 and 2). Both complexes were isolated, and the evidence for such a ruthenium−vinylene structure comes from the ^1H NMR spectra, in which two doublets of triplets of vinylene signals appear at 8.84 (J_{H-H} = 13.0 Hz) and 5.70 (J_{H-H} = 13.0 Hz) (for triethylsilylvinylene) and 8.52 (J_{H-H} = 12.6 Hz) and 5.80 (J_{H-H} = 12.6 Hz) (for triethylgermylvinylene). It is worth emphasizing that similarly to the catalytic transformation of terminal alkynes with vinylgermanes versus vinylsilanes, the stoichiometric reaction (3) takes twice as long as reaction (2), and therefore the GC-MS analysis showed much less unreacted ethynyltriethylgermane than the respective ethynyltriethylsilane.

The [Ru]−H complex is apparently a product of acetylene insertion into complex **IV** (followed by the elimination of the substituted ethyne compound) in three experiments (similarly to the insertion of acetylene into the [Ru]−Si bond[14a] and to

Table 1. Catalytic Transformation of Terminal Alkynes with Vinylgermanes: Reaction Catalyzed by Ruthenium Complexes I−V[a]



no.	GeR′$_3$	R	catalyst	yield [%] (TOF [h^{-1}])
1	GeEt$_3$	 [c]	**I**	88,[d] 70[g] (56 h^{-1})
2			**I**	47[f] (20 h^{-1})
3			**II**	80
4			**III**	54
5			**IV**	50
6			**V**	26
7		*t*-Bu	**I**	99[b]
8		Cy	**I**	37
9		Ph	**I**	0
10			**I**	0
11		*n*-C_5H_{11}	**I**	69, 57[g] (38 h^{-1})
12		SiEt$_3$	**I**	81, 54,[e] 75[g] (36 h^{-1})
13		Si(*i*-Pr)$_3$	**I**	74, 48,[e] 68[g]
14		Si(*t*-Bu)Me$_2$	**I**	50
15		SiMe$_2$Ph	**I**	47, 45[g]
16		GeEt$_3$	**I**	94,[c] 90[g] (58 h^{-1})
17	GeMe$_2$Ph	GeEt$_3$	**I**	90,[c] 83[g] (59 h^{-1})

[a] Reaction conditions unless stated otherwise: open system, toluene (0.5 M), t = 48 h, T = 110 °C, $[Ru]:[CH_2{=}CHGeR_3]:[CH{\equiv}CR] = 2 \times 10^{-2}:3:1$. [b]Closed system, t = 24 h, T = 100 °C. [c] t = 24h $[Ru]:[CH_2{=}CHGeR_3]:[CH{\equiv}CGeEt_3] = 2 \times 10^{-2}:2:1$. [d]$t$ = 24h. [e] $[Ru]:[CH_2{=}CHGeR_3]:[CH{\equiv}CR] = 2 \times 10^{-2}:2:1$, accompanied by traces of alkyne dimerization product. [f]$[Ru]:[CH_2{=}CHGeR_3]:[CH{\equiv}CR] = 10^{-2}:3:1$. [g]Isolated yield. The product yields were determined by GC. Initial TOF measured after 0.5 h of reaction and expressed by moles of alkyne per mole of [Ru] per hour.

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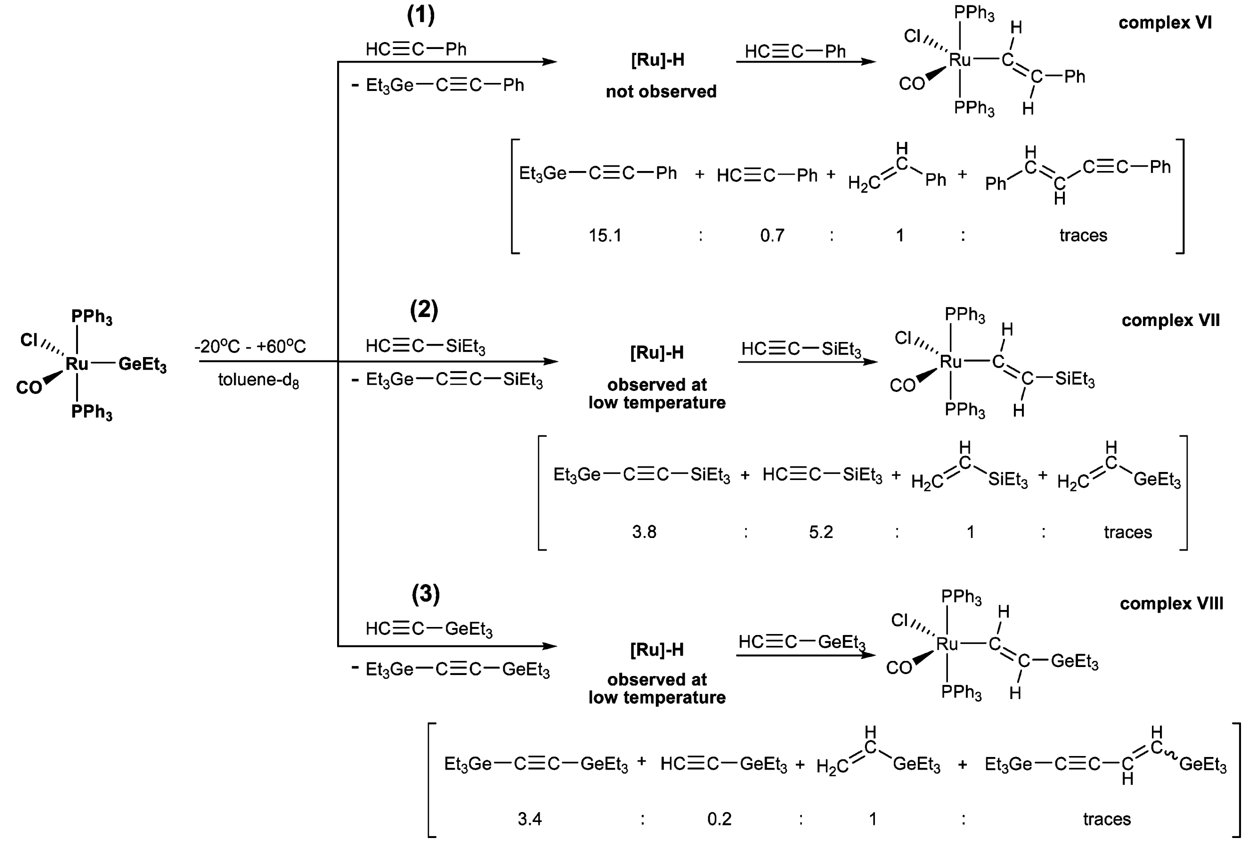
Scheme 3. Reaction of Equimolar Amounts of IV with Acetylenes



the insertion of olefins into the [Ru]−Ge[11] and [Ru]−Si[10] bonds). However, in the absence of vinylgermane this complex is active in the hydrogenation of acetylenes as well as its respective dimerization and co-dimerization with styrene as a result of the well-known reactions catalyzed by ruthenium complexes.[16]

Vinylene complexes of ruthenium **VI**−**VIII** were isolated, and their structures were confirmed by ^{1}H NMR and by comparison with those previously reported.[14a,17,18]

Contrary to the stoichiometric experiments (under catalytic conditions (100−110 °C)), vinylgermane, particularly if added in excess, reacted preferentially with the ruthenium hydride complex according to a well-documented process to yield the [Ru]−Ge complex and ethylene,[11] which explains the catalytic activity of both [Ru]−H and [Ru]−Ge systems in the germylative coupling of alkynes. Apparently, similarly to silylative coupling of acetylenes[14a] in the case of phenylacetylene, its reaction with the [Ru]−H occurs more rapidly than with the [Ru]−Ge complex, giving vinylene complex **VI**, and germylation of phenylacetylene is not observed under the conditions studied.

The results of the above experiments on germylation of acetylenes and their previously reported silylation allow us to propose a unified mechanism for the reaction of vinyl-substituted germanium and silicon compounds with selected substituted acetylenes (see Scheme 4).

The mechanistic scheme involves an insertion of alkynes into the [Ru]−E (E = Ge, Si) bond followed by β-H elimination to give substituted ethynes and subsequently the well-documented insertion of vinylgermanium (vinylsilicon) compounds into the [Ru]−H bond followed by β-E (E = Ge, Si) elimination of ethylene. Dissociation of phosphine is postulated to generate the active Ru catalysts.

This general mechanism is proved by the stoichiometric studies of the insertion of vinylsilicon[10] and vinylgermanium[11] compounds into the [Ru]−H bond as well as the above-described insertion of acetylenes into [Ru]−Ge and, as previously reported, also into [Ru]−Si bonds.[14a]

Experimental Section

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 $C_6D_5CD_3$) solution. Chemical shifts are reported in δ (ppm) with reference to the residue portion solvent (CH_3Cl) peak for ^{1}H and ^{13}C. 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 2100T, 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). 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

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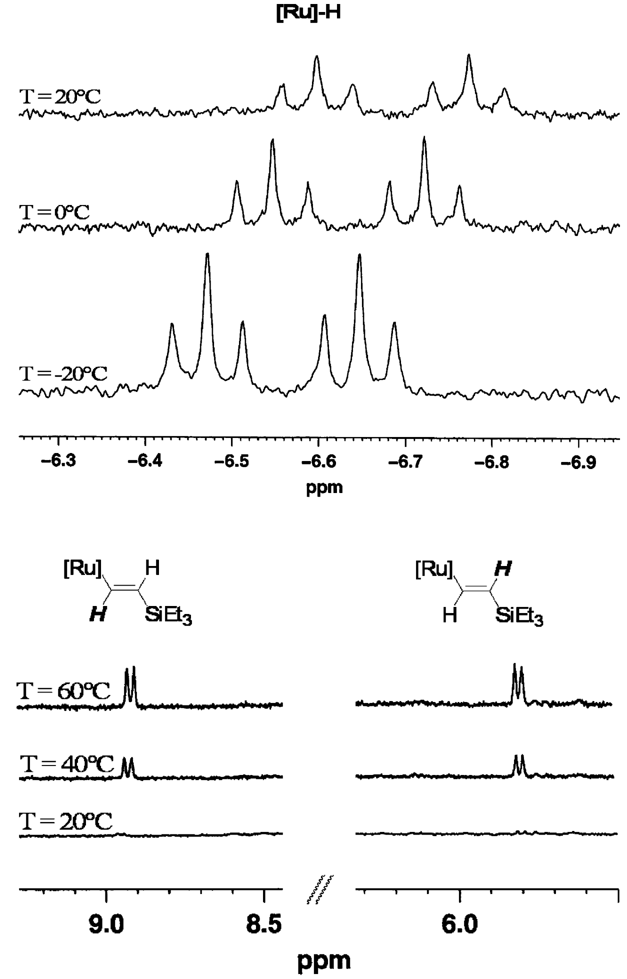


Figure 1. Temperature dependence of the ^{1}H NMR spectra in the reaction of **IV** with $HC{\equiv}CSiEt_3$.

degassed by bulb-to-bulb distillation. All the reactions were carried out under dry argon.

Materials. The chemicals were obtained from the following sources: toluene, dodecane, pentane, and hexane were purchased from Fluka; $CDCl_3$ and $C_6D_5CD_3$ from Dr Glaser A.G. Basel. Triethylbromogermane and phenyldimethylbromogermane were purchased from GELEST. The substituted acetylenes were bought from Aldrich. $CH_2{=}CHGeEt_3$ and $CH_2{=}CHGeMe_2Ph$ were prepared according to literature procedures.[11] The ruthenium complexes $[RuHCl(CO)(PCy_3)_2]$ (**I**), $[RuHCl(CO)(P\textit{i}\text{-}Pr_3)_2]$ (**II**), $[RuHCl(CO)(PPh_3)_3]$ (**III**), $[Ru(GeEt_3)Cl(CO)(PPh_3)_2]$ (**IV**), and $[RuH(CO)(MeCN)_2(PCy_3)_2]^+[BF_4]^-$ (**V**) were prepared according to literature procedures.[11,19] 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.

Synthesis of Ethynyltriethylgermane [$Et_3Ge{\equiv}CH$]. In a Schlenk tube equipped with magnetic stirrer 2.89 g (12.06 mmol) of bromotriethylgermane and 60 mL of dried and deoxidized THF were placed under argon, then 29 mL of the $CH{\equiv}CMgBr$ (1.0 mol/L) THF solution was added dropwise. The reaction mixture was kept for 24 h at 45 °C while stirring the contents with a magnetic stirrer. After this time the reaction mixture was washed with water and diethyl ether three times and dried over $CaCl_2$. The ethynyltriethylgermane was purified by distillation (bp 115 °C, yield 82%).

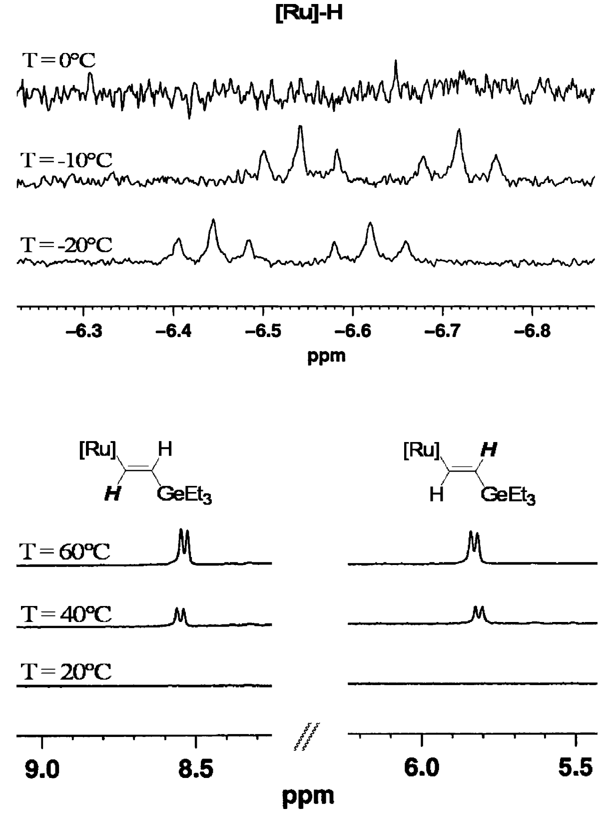
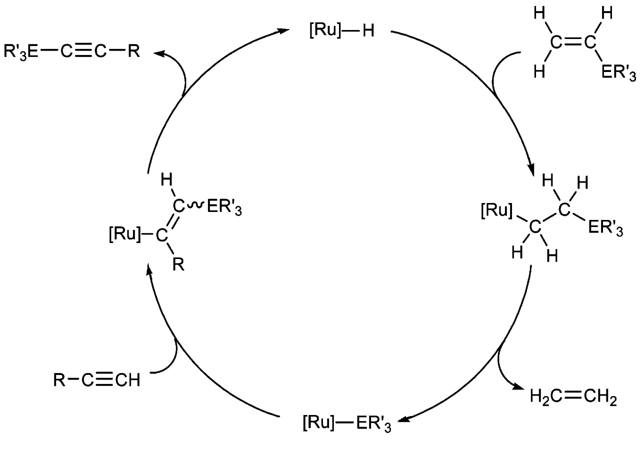


Figure 2. Temperature dependence of the ^{1}H NMR spectra in the reaction of **IV** with $HC{\equiv}CGeEt_3$.

Scheme 4. Mechanism of Coupling of Alkynes with Vinyl-Substituted Organometallic Compounds



E = Ge, Si

Analytic data: ^{1}H NMR ($CDCl_3$; δ (ppm)): 0.88 (q, 6H, $GeCH_2CH_3$, $J_{H-H} = 8.1$ Hz), 1.09 (t, 9H, $GeCH_2CH_3$, $J_{H-H} = 8.1$ Hz), 2.28 (s, 1H, CH). ^{13}C NMR ($CDCl_3$; δ (ppm)): 5.67 ($GeCH_2CH_3$), 8.96 ($GeCH_2CH_3$), 87.67 ($Ge{-}C{\equiv}CH$), 93.11 ($Ge{-}C{\equiv}CH$). MS (EI) [*m/z* (%)]: 157 ($M^{+\bullet} - CH_2CH_3$, 100), 129 (89), 113 (3), 99 (43), 89 (11), 73 (7). This type of compound is known from the literature.[20] However, the method used is analogous to the one described in the case of vinyltriethylgermane.[11]

Reaction of Equimolar Amounts of $[Ru(GeEt_3)Cl(CO)(PPh_3)_2]$ with Acetylenes. In a typical test, the ruthenium catalyst $[Ru(GeEt_3)Cl(CO)(PPh_3)_2]$ was dissolved in $[D_8]$toluene and placed in an NMR ampule under argon. The ampule was cooled in liquid

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(20) (a) Eastmond; R.; Walton, D. R. M. *Tetrahedron* **1972**, *28*, 4591−4599. (b) Marerolles *Bull. Soc. Chim. Fr.* **1960**, 859.

nitrogen, then acetylene was added (at the molar ratio [Ru]:[acetylene] = 1:1.2). After that, the ampule was inserted into a Brucker Ultra Shield spectrometer (600 MHz) and slowly heated. The spectra were recorded at various temperatures between −20 and +60 °C with 10 °C gradation of temperature.

Representative Procedure for Synthesis of [$\mathrm{Et_3Ge{-}C{\equiv}C{-}R}$]. In a typical experiment, the ruthenium catalyst [$\mathrm{RuHCl(CO)(PCy_3)_2}$] (2 mol %) was dissolved in toluene and placed in a glass ampule under argon. The reagents and decane as internal standard (5% by volume all components), vinyltriethylgermane, and the acetylene (usually used in the molar ratio [Ru]:[$\mathrm{CH_2{=}CHGeEt_3}$]:[$\mathrm{CH{\equiv}CR}$] = 2×10^{-2}:3:1 or 2×10^{-2}:1:2) were added. Subsequently, the ampule was heated to 100 or 110 °C and maintained at that temperature for 24−48 h. The progress of the reaction was monitored by GC and GC-MS. The final products were separated from the residues of the catalyst and reactants by purification on an $\mathrm{SiO_2}$ column (modified with 15% of $\mathrm{Et_3N}$ when needed) with hexane as eluent. All products of catalytic transformation of terminal alkynes with vinylgermanes were oily liquids.

Analytic Data: 1-(*tert*-Butyl)-2-(triethylgermyl)ethyne. ^{1}H NMR ($\mathrm{CDCl_3}$; δ (ppm)): 0.81 (q, 6H, $\mathrm{GeC}H_2\mathrm{CH_3}$, $J_{\mathrm{H-H}} = 8{,}1$ Hz), 1.15 (t, 9H, $\mathrm{GeCH_2C}H_3$, $J_{\mathrm{H-H}} = 8{,}1$ Hz), 1.22 (s, 9H, $(\mathrm{C}H_3)_3\mathrm{C}$), ^{13}C NMR ($\mathrm{CDCl_3}$; δ (ppm)): 5.81 ($\mathrm{Ge}C\mathrm{H_2CH_3}$), 9.20 ($\mathrm{GeCH_2}C\mathrm{H_3}$), 29.01 ($(\mathrm{CH_3})_3\mathrm{C}$); 30.82 ($(C\mathrm{H_3})_3\mathrm{C}$), 83.5 ($\mathrm{Ge{-}C{\equiv}}C$), 108.74 ($\mathrm{Ge{-}}C\mathrm{{\equiv}C}$). MS (EI) [*m/z* (%)]: 226 ($[\mathrm{M+H}]^{+\bullet} - \mathrm{CH_3}$, 1), 213 ($\mathrm{M}^{+\bullet} - \mathrm{CH_2CH_3}$, 100), 184 (9), 157 (29), 139 (6), 129 (5), 113 (9), 101 (8), 79 (4), 68 (4), 53 (3). Anal. Calcd (%) for $\mathrm{C_{12}H_{24}Ge}$: C 59.81, H 10.04. Found: C 59.90, H 10.11. Isolated yield: 80%.

1-(Cyclohexyl)-2-(triethylgermyl)ethyne. ^{1}H NMR ($\mathrm{CDCl_3}$; δ (ppm)): 0.83 (q, 6H, $\mathrm{GeC}H_2\mathrm{CH_3}$, $J_{\mathrm{H-H}} = 8.1$ Hz), 1.11 (t, 9H, $\mathrm{GeCH_2C}H_3$, $J_{\mathrm{H-H}} = 8.1$ Hz), 1.2−2.6 (m, 11H, $\mathrm{C_6}H_{11}$). ^{13}C NMR ($\mathrm{CDCl_3}$; δ (ppm)): 5.75 ($\mathrm{Ge}C\mathrm{H_2CH_3}$), 9.20 ($\mathrm{GeCH_2}C\mathrm{H_3}$), 24.8−32.6 ($C_6\mathrm{H_{11}}$), 82.6 ($\mathrm{Ge{-}C{\equiv}}C$), 107.7 ($\mathrm{Ge{-}}C\mathrm{{\equiv}C}$). MS (EI) [*m/z* (%)]: 238 ($[\mathrm{M+H}]^{+\bullet} - \mathrm{CH_2CH_3}$, 100), 211 (38), 181 (23), 153 (6), 125 (7), 105 (11), 79 (17), 55 (4). Anal. Calcd (%) for $\mathrm{C_{14}H_{26}Ge}$: C 62.98, H 9.82. Found: C 61.85, H 9.99. Isolated yield: 34%.

1-(*n*-Pentyl)-2-(triethylgermyl)ethyne. ^{1}H NMR ($\mathrm{CDCl_3}$; δ (ppm)): 0.80−2.2 (m, 26H, $\mathrm{C}H_2$, $\mathrm{C}H_3$). ^{13}C NMR ($\mathrm{CDCl_3}$; δ (ppm)): 5.88 ($\mathrm{Ge}C\mathrm{H_2CH_3}$), 9.05 ($\mathrm{GeCH_2}C\mathrm{H_3}$), 19.94 ($C\mathrm{H_2}$), 22.25 ($C\mathrm{H_2}$), 22.65 ($C\mathrm{H_2}$), 28.76 ($C\mathrm{H_2}$), 30.99 ($C\mathrm{H_3}$), 88.77 ($\mathrm{Ge{-}C{\equiv}}C$), 107.74 ($\mathrm{Ge{-}}C\mathrm{{\equiv}C}$). MS (EI) [*m/z* (%)]: 227 ($\mathrm{M}^{+\bullet} - \mathrm{CH_2CH_3}$, 100), 199 (64), 171 (19), 139 (6), 127 (5), 113 (11), 95 (31), 77 (5), 67 (8), 55 (2). Anal. Calcd (%) for $\mathrm{C_{13}H_{26}Ge}$: C 61.23, H 10.28. Found: C 61.12, H 10.19. Isolated yield: 57%.

1-(Triethylsilyl)-2-(triethylgermyl)ethyne. ^{1}H NMR ($\mathrm{CDCl_3}$; δ (ppm)): 0.59 (q, 6H, $\mathrm{SiC}H_2\mathrm{CH_3}$), 0.84 (q, 6H, $\mathrm{GeC}H_2\mathrm{CH_3}$, $J_{\mathrm{H-H}} = 8{,}1$ Hz), 1.01 (t, 9H, $\mathrm{SiCH_2C}H_3$), 1.10 (t, 9H, $\mathrm{GeCH_2C}H_3$, $J_{\mathrm{H-H}} = 8{,}1$ Hz). ^{13}C NMR ($\mathrm{CDCl_3}$; δ (ppm)): 4.65 ($\mathrm{Si}C\mathrm{H_2CH_3}$), 5.90 ($\mathrm{Ge}C\mathrm{H_2CH_3}$), 7.59 ($\mathrm{SiCH_2}C\mathrm{H_3}$), 9.07 ($\mathrm{GeCH_2}C\mathrm{H_3}$), 111.17 ($\mathrm{Ge{-}}C\mathrm{{\equiv}C}$), 112.56 ($\mathrm{Si{-}}C\mathrm{{\equiv}C}$). MS (EI) [*m/z* (%)]: 271 ($\mathrm{M}^{+\bullet} - \mathrm{CH_2CH_3}$, 100), 244 (16), 215 (9), 185 (9), 157 (13), 127 (8), 103 (3), 83 (2), 60 (5). Anal. Calcd (%) for $\mathrm{C_{14}H_{30}GeSi}$: C 56.22, H 10.11. Found: C 56.32, H 9.99. Isolated yield: 75%.

1-(Triisopropylsilyl)-2-(triethylgermyl)ethyne. ^{1}H NMR ($\mathrm{CDCl_3}$; δ (ppm)): 0.84 (q, 6H, $\mathrm{GeC}H_2\mathrm{CH_3}$, $J_{\mathrm{H-H}} = 8.1$ Hz), 1.03−1.13 (m, 30H, $\mathrm{C}H$, $\mathrm{C}H_2$, $\mathrm{C}H_3$). ^{13}C NMR ($\mathrm{CDCl_3}$; δ (ppm)): 5.97 ($\mathrm{Ge}C\mathrm{H_2CH_3}$), 9.14 ($\mathrm{GeCH_2}C\mathrm{H_3}$), 11.27 ($C\mathrm{H}$), 18.70 ($\mathrm{SiCH(}C\mathrm{H_3)_2}$), 109.80 ($\mathrm{Ge{-}}C\mathrm{{\equiv}C}$), 112.97 ($\mathrm{Si{-}}C\mathrm{{\equiv}C}$). MS (EI) [*m/z* (%)]: 313 ($\mathrm{M}^{+\bullet} - \mathrm{CH_2CH_3}$, 14), 299 (80), 271 (100), 243 (68), 229 (65), 215 (42), 201 (60), 185 (19), 171 (44), 143 (17), 129 (18), 101 (24), 87 (13), 73 (24), 59 (19). Anal. Calcd (%) for $\mathrm{C_{17}H_{36}GeSi}$: C 59.84, H 10.63. Found: C 59.75, H 10.49. Isolated yield: 68%.

1-(*tert*-Butyldimethylsilyl)-2-(triethylgermyl)ethyne. ^{1}H NMR ($\mathrm{CDCl_3}$; δ (ppm)): 0.17 (s, $\mathrm{C}H_3\mathrm{((CH_3)_3C)SiC{\equiv}}$); 0.96 (s, $\mathrm{CH_3((C}H_3\mathrm{)_3C)SiC{\equiv}}$); 0.86 (q, 6H, $\mathrm{GeC}H_2\mathrm{CH_3}$, $J_{\mathrm{H-H}} = 8{,}1$ Hz), 1.12 (t, 9H, $\mathrm{GeCH_2C}H_3$, $J_{\mathrm{H-H}} = 8{,}1$ Hz). ^{13}C NMR ($\mathrm{CDCl_3}$; δ (ppm)): −4.54 ($C\mathrm{H_3((CH_3)_3C)SiC{\equiv}}$), 5.85 ($\mathrm{Ge}C\mathrm{H_2CH_3}$), 9.25 ($\mathrm{GeCH_2}C\mathrm{H_3}$), 16.62 ($\mathrm{CH_3((CH_3)_3}C\mathrm{)SiC{\equiv}}$), 26.13 ($\mathrm{CH_3((}C\mathrm{H_3)_3C)SiC{\equiv}}$), 112.12, 114.40 ($\mathrm{Si}C{\equiv}C\mathrm{Ge}$). MS (EI) [*m/z* (%)]: 271 ($\mathrm{M}^{+\bullet} - \mathrm{CH_2CH_3}$, 99), 243 (100), 215 (69), 188 (31), 188 (31), 173 (7), 157 (33), 143 (4), 131 (13), 111(14), 87 (10), 73 (31), 57 (11). Anal. Calcd (%) for $\mathrm{C_{14}H_{30}GeSi}$: C 56.22, H 10.11. Found: C 56.39, H 9.89. Isolated yield: 45%.

1-(Phenyldimethylsilyl)-2-(triethylgermyl)ethyne. ^{1}H NMR ($\mathrm{CDCl_3}$; δ (ppm)): 0.41 (s, 6H, $\mathrm{SiC}H_3$), 0.86 (q, 6H, $\mathrm{GeC}H_2\mathrm{CH_3}$, $J_{\mathrm{H-H}} = 8{,}1$ Hz), 0.92 (t, 9H, $\mathrm{GeCH_2C}H_3$, $J_{\mathrm{H-H}} = 8{,}1$ Hz), 7.36−7.69 (m, 5H, $\mathrm{C}H$). ^{13}C NMR ($\mathrm{CDCl_3}$; δ (ppm)): −0.37 ($\mathrm{Si}C\mathrm{H_3}$), 5.85 ($\mathrm{Ge}C\mathrm{H_2CH_3}$), 9.08 ($\mathrm{GeCH_2}C\mathrm{H_3}$), 111.58 ($\mathrm{Ge{-}}C\mathrm{{\equiv}C}$), 113.88 ($\mathrm{Si{-}}C\mathrm{{\equiv}C}$), 127.65 ($C\mathrm{H}$), 129.11 ($C\mathrm{H}$), 133.62 ($C\mathrm{H}$), 137.37 ($c_i$-$\mathrm{C_6H_5}$). MS (EI) [*m/z* (%)]: 319 (M^+, 3), 291 ($\mathrm{M}^{+\bullet} - \mathrm{CH_2CH_3}$, 100), 263 (65), 235 (22), 171 (3), 159 (12), 145 (13), 105 (8), 89 (4), 75 (8), 53 (4). Anal. Calcd (%) for $\mathrm{C_{16}H_{26}GeSi}$: C 60.22, H 8.21. Found: C 60.04, H 8.29. Isolated yield: 45%.

1-(Triethylgermylethynyl)-1-trimethylsiloxycyclohexane. ^{1}H NMR ($\mathrm{CDCl_3}$; δ (ppm)): 0.19 (s, 9H, $\mathrm{SiC}H_3$), 0.85 (q, 6H, $\mathrm{GeC}H_2\mathrm{CH_3}$, $J_{\mathrm{H-H}} = 8{,}1$ Hz), 1.09 (t, 9H, $\mathrm{GeCH_2C}H_3$, $J_{\mathrm{H-H}} = 8{,}1$ Hz), 1.47−1.85 (m, 10H, $\mathrm{C}H_2$). ^{13}C NMR ($\mathrm{CDCl_3}$; δ (ppm)): 2.13 ($\mathrm{Si}C\mathrm{H_3}$), 5.64 ($\mathrm{Ge}C\mathrm{H_2CH_3}$), 8.99 ($\mathrm{GeCH_2}C\mathrm{H_3}$), 23.36 ($C\mathrm{H_2}$), 25.34 ($C\mathrm{H_2}$), 41.55 ($C\mathrm{H_2}$), 70.45 ($c_i$-$\mathrm{C_6H_{10}}$), 87.17 ($\mathrm{Ge{-}C{\equiv}}C$), 110.35 ($\mathrm{Ge{-}}C\mathrm{{\equiv}C}$). MS (EI) [*m/z* (%)]: 328 ($\mathrm{M}^{+\bullet} - \mathrm{CH_2CH_3}$, 79), 311 (42), 300 (38), 271 (43), 224 (9), 209 (26), 196 (39), 181 (46), 161 (24), 147 (22), 133 (21), 117 (23), 101 (19), 74 (100), 60 (10), 48 (39). Anal. Calcd (%) for $\mathrm{C_{17}H_{34}GeOSi}$: C 57.49, H 9.65. Found: C 57.56, H 9.60. Isolated yield: 70%.

1,2-Bis(triethylgermyl)ethyne. ^{1}H NMR ($\mathrm{CDCl_3}$; δ (ppm)): 0.84 (q, 12H, $\mathrm{GeC}H_2\mathrm{CH_3}$, $J_{\mathrm{H-H}} = 8{,}1$ Hz), 1.10 (t, 18H, $\mathrm{GeCH_2C}H_3$, $J_{\mathrm{H-H}} = 8{,}1$ Hz). ^{13}C NMR ($\mathrm{CDCl_3}$; δ (ppm)): 4.65 ($\mathrm{Si}C\mathrm{H_2CH_3}$), 5.98 ($\mathrm{Ge}C\mathrm{H_2CH_3}$), 9.07 ($\mathrm{GeCH_2}C\mathrm{H_3}$), 110.75 ($\mathrm{Ge{-}}C{\equiv}C\mathrm{{-}Ge}$). MS (EI) [*m/z* (%)]: 315 ($\mathrm{M}^{+\bullet} - \mathrm{CH_2CH_3}$, 100), 287 (51), 258 (30), 231 (16), 199 (9), 171 (14), 157 (6), 129 (10), 101 (11), 75 (5). Anal. Calcd (%) for $\mathrm{C_{14}H_{30}Ge_2}$: C 48.93, H 8.80. Found: C 48.89, H 8.77. Isolated yield: 90%.

1-(Phenyldimethylgermyl)-2-(triethylgermyl)ethyne. ^{1}H NMR ($\mathrm{CDCl_3}$; δ (ppm)): 0.56 (s, 6H, $\mathrm{GeC}H_3$), 0.89 (q, 6H, $\mathrm{GeC}H_2\mathrm{CH_3}$, $J_{\mathrm{H-H}} = 8.1$ Hz), 1.11 (t, 9H, $\mathrm{GeCH_2C}H_3$, $J_{\mathrm{H-H}} = 8.1$ Hz), 7.35−7.62 (m, 5H, $\mathrm{C}H$). ^{13}C NMR ($\mathrm{CDCl_3}$; δ (ppm)): −0.50 ($\mathrm{Ge}C\mathrm{H_3}$), 5.91 ($\mathrm{Ge}C\mathrm{H_2CH_3}$), 9.09 ($\mathrm{GeCH_2}C\mathrm{H_3}$), 110.86, 111.31 ($\mathrm{Ge{-}}C\mathrm{{\equiv}C}$), ($\mathrm{Ge{-}}C\mathrm{{\equiv}C}$), 127.95 ($C\mathrm{H}$), 129.66 ($C\mathrm{H}$), 132.98 ($C\mathrm{H}$), 139.18 ($c_i$-$\mathrm{C_6H_5}$). MS (EI) [*m/z* (%)]: 335 ($\mathrm{M}^{+\bullet} - \mathrm{CH_2CH_3}$, 100), 307 (33), 277 (17), 245 (2), 175 (10), 151 (10), 132 (3), 89 (8), 75 (4), 51 (6). Anal. Calcd (%) for $\mathrm{C_{16}H_{26}Ge_2}$: C 52.84, H 7.21. Found: C 52.93, H 7.27. Isolated yield: 83%.

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