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Synthesis of substituted vinylgermanes and germylsilylethenes via ruthenium complex catalyzed germylation of olefins

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A series of substituted vinylgermanes and divinylgermanes have been synthesized in moderate or high yield via two reactions of olefins and dienes catalyzed by [RuHCl(CO) (PCy$_3$)$_2$], i.e. germylative coupling with vinylgermanes and dehydrogenative germylation with hydrogermanes. While the former reaction can be a versatile way of regioselective synthesis of products (particularly useful for the stereoselective synthesis of germylsilylethenes), the latter could be used as a complement, especially in synthesis of germylate dioxol ethene and vinyl ethers. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: germanes; ruthenium complex; catalysts germylation

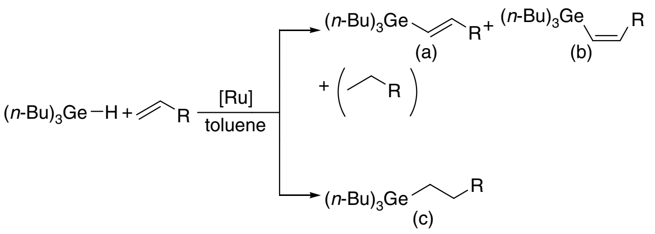
Introduction

Unsaturated organogermanium compounds have recently become of great interest as important reagents for organic synthesis due to their very low toxicity compared with that of the respective organotin compounds.[1,2] The most commonly used methods for the synthesis of vinyl-substituted germanes involve the use of alkenyl metals or alkynes and alkynylgermanes [for review see references[3,4]]. Hydrogermylation of alkynes is the most important route to vinylgermanes and it can be realized either with the use of a radical initiator or transition metal (TM) complexes as catalysts, resulting in the formation of three isomers (*E*, *Z* and *gem*) with selectivity determined by both electronic and steric properties of substituents in the reaction partners, type of solvent and characteristics of the catalyst.[5]

While in the last two decades two new reactions of silicon derivatives catalyzed by TM metal complexes have been developed to provide universal routes for synthesis of organosilicon compounds of vinylsilicon functionality, i.e. silylation of olefins with hydrosilanes (dehydrogenative silylation) and silylation with vinylsilanes (silylative coupling) [for review see reference[6]], only two reports on respective reactions of olefin germylation with hydrogermanes[7] and vinylgermanes[8] have recently appeared. By analogy to the respective silylation reactions, these two processes proceed in the presence of catalytic species containing initially or generating *in situ* M–H and M–Ge bonds (where M = Ru, Rh) via cleavage of the =C–H bond of olefins and =C–Ge and H–Ge of germanes. Therefore, the aim of this work was to use these two new catalytic transformations for selective synthesis of a variety of compounds with vinylgermanium functionality.

Results and Discussion

The dehydrogenative germylation catalyzed by ruthenium complexes containing Ru–H bond occurs according to Eq. (1) and is mostly accompanied by the products of hydrogermylation:



(1)

Seki and Murai's group[7] reported on the stereoselective dehydrogenative germylation of styrene catalyzed by Ru$_3$(CO)$_{12}$ (toluene, reflux, 3 h, 10-fold excess of styrenes, 91% *E* product) as well as of *para*-substituted styrenes (but in moderate yield, 56–66%).[7]

Our experiments have shown that [RuHCl(CO)(PCy$_3$)$_2$] is the most efficient catalyst of dehydrogenative germylation of a variety of olefins occurring at 110 °C but accompanied by hydrogermylation products (see Table 1).

Dehydrogenative germylation of styrene, vinylpyrrolidinone, vinylcarbazole and vinylcyclohexane epoxide (entries 1–4) with tributylgermane proceeds stereo and regioselectively to give exclusively *E*-isomers [Eq. (1), a]. Only for vinyl butyl ether and vinyldioxolane (entries 5 and 6) was a mixture of *E* and *Z* products [Eq. (1), a, b] with a preference for the *E*-isomer observed. Moreover, the reaction of hydrogermanes with vinylsilanes (entries 7 and 8) and vinylgermanes (entry 9) (via hydrogermylation) almost exclusively led to saturated products [Eq. (1), c].

Although the dehydrogenative germylation of olefins seems to be as effective as previously reported germylative coupling

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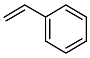
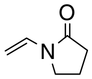
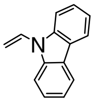
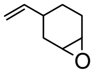
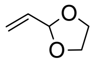
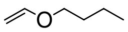
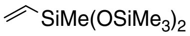
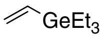
Table 1. Catalytic transformation of tri-*n*-butylgermane *via* dehydrogenative germylation of olefins catalyzed by $[RuHCl(CO)(PCy_3)_2]$

No.	R	Conversion $(n\text{-}Bu)_3GeH$ (%)	Selectivity a/b/c (%)	Isolated yield (%)	Isolated yield via germylative coupling (%)[8]
1		99	92/0/8	84 (*E*)	93 (*E*)
2		34	54/0/46		83 (*E*)
3		84	81/0/19	63 (*E*)	78 (*E*)
4		13	51/0/49		
5		96	84/12/4	85 (*E*)	
6		37, 99[a]	61/31/6[b]	89 (*E* + *Z*)	84 (*E* + *Z*)
7		92	9/0/91		
8		98	2/0/98		
9		90	4/2/92[b]		

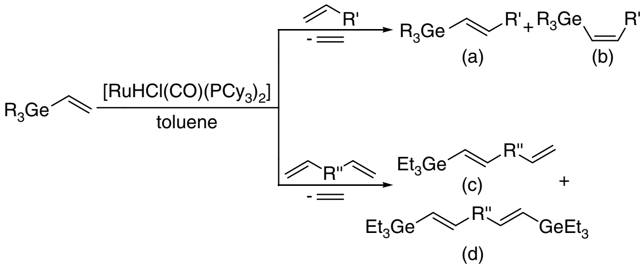
Reaction conditions: open system, toluene (0.5 M), $t = 8$ h, temperature = 110 °C. $[RuHCl(CO)(PCy_3)_2]:[(n\text{-}Bu)_3GeH]:[RCH{=}CH_2] = 10^{-2}:1:3$. [a] $10^{-2}:1:10$, 100 °C. [b] Accompanied by traces of *gem*-product.

of olefins with terminal vinylgermanes,[8] the former reaction is accompanied by formation of respective alkanes. In contrast, the latter, also catalyzed by ruthenium complexes such as $[RuHCl(CO)(PCy_3)_2]$ and $[RuHCl(CO)(PPh_3)_3]$, occurs with selected alkenes, leading to effective formation of substituted vinylgermanes according to [Eq. (2)].

A separate equimolar study on insertion of vinylgermane into the Ru–H bond as well as the insertion of styrene into the Ru–Ge bonds have supported the mechanism proposed in Marciniec *et al.*[8]

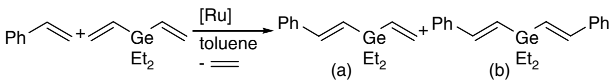
We recently reported the cross-coupling of vinylgermanes with styrene, *p*-substituted styrenes, vinylpyrrolidinone and vinylcarbazole to give stereoselectively *E*-products and with vinyl butyl ether to yield *E* + *Z* products (see Table 1).

Now we present the catalytic cross-coupling of vinylgermane with other olefins and vinylsilane occurring with moderate conversion and yield but giving, in case of vinylsilane, exclusively *E*-products [Eq. (2), a], which cannot be synthesized by other methods. Reactions of vinylgermanes with exemplary dienes led to a high yield but of a mixture of mono- and digermylsubstituted dienes [Eq. (2), c, d; see Table 2].



(2)

On the other hand, the reactions of divinyldiethylgermane with styrene produced respective mono- and di-substituted vinylgermanes with the advantages of monosubstituted ones [Eq. (3) and Table 3].



(3)

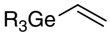
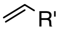
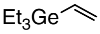
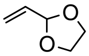
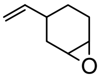
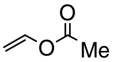
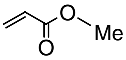
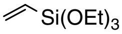
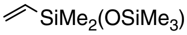
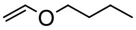
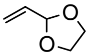
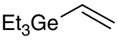
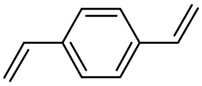
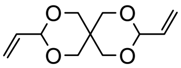
Selected functionalized vinylgermanes synthesized via the above methods (see Tables 1–3) were isolated according to the procedures described in the Experimental section. Non-isolated products were identified on the basis of GC-MS spectra.

The reaction of vinylgermanes with vinylsilanes can be efficiently used for stereoselective synthesis of *E*-germylsilylethenes, which cannot be obtained by dehydrogenative germylation, silylation and cross-metathesis methods. In order to confirm the catalytic route via silylative or germylative coupling, we have used the complexes $[Ru(GeEt_3)Cl(CO)(PPh_3)_2]$ and $[Ru(SiMe_3)Cl(CO)(PPh_3)_2]$ in equimolar reactions with vinylsilanes and vinylgermanes.

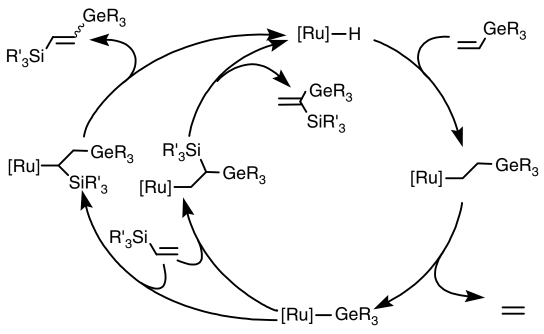
The results of these stoichiometric experiments proved that the cross-coupling of vinylgermanium with vinylsilanes involves an insertion of vinylgermane into the Ru–H bond followed by β-Ge elimination of ethylene and the migratory insertion of vinylsilanes into the Ru–Ge bond followed by β-H elimination to give silylgermylethene (see Scheme 1).

It is noteworthy that germylative coupling of olefins and dienes with vinylgermanes appeared to be a means for regioselective synthesis of products with moderate yield and, for vinylsilanes, stereoselectivity (*E*-product). This method is particularly useful for the synthesis of germylsilylethenes. On the other hand, the

Table 2. Catalytic transformation of vinylgermanes via *cross*-coupling with olefins and dienes catalyzed by $[RuHCl(CO)(PCy_3)_2]$

No.			Temperature (°C)	Yield by GC (%)	Selectivity a/b (%)	Isolated yield (%)
10			100	64^{c}	50/50	
11			110	59	100/0	59 (*E*)
12			100	0	–	
13			100	7	100/0	
14			110	$69^{a,b}$	$100/0^{d}$	51 (*E*)
15			110	31	$100/0^{d}$	
16			120	20	$100/0^{d}$	
17			110	60	$95/0^{d,e}$	45 (*E*)
18			110	38	$100/0^{d}$	
19			80	61^{b}	45/55	45 (*E* + *Z*)
20			110	72^{a}	55/45	60 (*E* + *Z*)
21			120	$14^{a,b}$	$100/0^{d}$	
					Selectivity c/d (%)	
22			100	84	40/60	31/44
23			100	99	20/80	–/68

Reaction conditions: open system, toluene (0.5 M), $t = 24$ h.
$[Ru]:[R_3GeCH{=}CH_2]:[R'CH{=}CH_2] = 2 \times 10^{-2}:1:3$, $[Ru]:[Ge]:[R'(CH{=}CH_2)_2] = 2 \times 10^{-2}:6:1$, $t = 48$ h or for vinylsilanes: $[Ru]:[R_3GeCH{=}CH_2]:[R'_3SiCH{=}CH_2] = 2 \times 10^{-2}:1:5$. [a] Closed systems. [b] $[Ru]:[R_3GeCH_2{=}CH]:[R'CH{=}CH_2] = 2 \times 10^{-2}:1:10$. [c] $[Ru]:[R_3GeCH{=}CH_2]:[R'CH_2{=}CH] = 3 \times 10^{-2}:1:10$. [d] Accompanied by product of *homo*-coupling of vinylsilane. [e] Accompanied by traces of *gem*-product.



Scheme 1. Catalytic scheme of germylation of vinylsilanes with vinylgermanes.

Table 3. Catalytic transformation of diethyldivinylgermane via *cross* coupling with styrene catalyzed by $[RuHCl(CO)(PCy_3)_2]$

[Ru]:[Ge]: [styrene]	Time (h)	Yield by GC (%)	Selectivity a/b (%)	Isolated yield (%)
$10^{-2}:1:4$	24	0	–	
$10^{-2}:1:6$	24	41	74/26	
	48	60	67/33	
$2 \cdot 10^{-2}:1:6$	24	52	71/29	
	48	73	60/40	40/25 (no. 24 and 25)

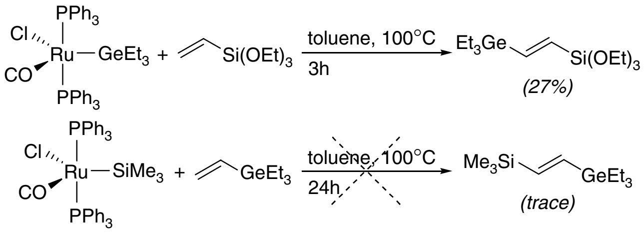
Reaction conditions: open system, toluene (0.5 M), $t = 48$ h, temperature = 110 °C.

germylation with hydrogermanes could be used as a complement, especially in the synthesis of germylated dioxol-ethene and vinyl ethers. Effective germylation of styrene by divinylgermanes can be applied for the synthesis of divinylfunctionalized germanes. Only traces of *gem*-isomers have been detected in both types of reactions.

Experimental

General methods

^{1}H-NMR (300 M Hz), ^{13}C-NMR (75 M Hz) ^{29}Si-NMR (60 M Hz) and DEPT spectra were recorded on a Varian XL 300 M Hz spectrometer in $CDCl_3$ (or $C_6D_5CD_3$) solution. Chemical shifts are reported in δ (ppm) with reference to the solvent ($CHCl_3$)



(4)

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 Thermal Conductivity Detector (TCD). Mass spectra of the monomers and products were obtained by GCMS analysis [Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and an ion trap detector]. Thin-layer chromatography (TLC) was carried out 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 was dried by distillation from sodium 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.

Materials

The chemicals were obtained from the following sources: toluene, dodecane, pentane and hexane were purchased from Fluka; $CDCl_3$ and $C_6D_5CD_3$ were obtained from Dr Glaser A.G. Basel. The substituted acetylenes were bought from Aldrich. The $CH_2{=}CHGeEt_3$ was prepared according to the literature procedure.[8] The ruthenium complexes $[RuHCl(CO)(PCy_3)_2]$ (**I**), $[RuHCl(CO)(PPh_3)_3]$ (**II**) and $[Ru(SiMe_3)Cl(CO)(PPh_3)_2]$ (**III**) were prepared according to the literature procedure.[9]

Synthesis of diethyldivinylgermane [$Et_2Ge(HC{=}CH_2)_2$]

In a Schlenk's tube equipped with a magnetic stirrer, 7 g (34.70 mmol) of diethyldichlorogermane and 120 ml of dried and deoxidized THF were placed under argon, then 80 ml of the $CH_2{=}CHMgBr$ (1.0 mol/l) THF solution was added dropwise. The reaction mixture was kept for 24 h at 45 °C with stirring. Then the reaction mixture was washed three times with water and diethylether and dried over $CaCl_2$. The diethyldivinylgermane was purified by distillation (b.p. 110 °C, yield 90%). Analytic data: ^{1}H NMR [$CDCl_3$; δ (ppm)]: 0.88 (q, 4H, J_{H-H} = 8.1 Hz, CH_2); 1.03 (t, 6H, J_{H-H} = 8.1 Hz, CH_3); 5.61–6.06 (dd, 2H, J_{H-H} = 3.6 Hz, J_{H-H} = 20.1 Hz, $GeCH{=}CH_2$); 6.27 (dd, 4H, J_{H-H} = 13.7 Hz, J_{H-H} = 6.3 Hz, $GeCH{=}CH_2$). ^{13}C NMR [$CDCl_3$; δ (ppm)]: 4.99 (CH_2); 8.86 (CH_3); 131.29 ($GeCH{=}CH_2$); 136.31 ($GeCH{=}CH_2$). MS (EI) [m/z (%)] = 157 ($M^{+\cdot} - CH_2CH_3$, 100), 129 (17), 101 (15). This compound was synthesized by the known method, analogous to the one described for vinyltriethylgermane.[8]

Representative procedure for the synthesis of [$(n\text{-}Bu)_3Ge{-}CH{=}CH\text{-}R$]

In a typical test, the ruthenium catalyst $[RuH(Cl)(CO)(PCy_3)_2]$ (1 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), tri-n-butylgermane and olefin {usually used at the molar ratio [Ru]:[$(n\text{-}Bu)_3GeH$]:[$CH_2{=}CHR$] = 10^{-2}:1 : 3 or 10^{-2}:1 : 10} were added. Then the ampoule was heated from 110 or 100 °C and maintained at that temperature for 8 h. The final products were separated from the residual catalyst and reagents using a column with silica. The progress of the reaction was controlled by GC and GCMS. All products of catalytic transformation of olefins with tri-n-butylgermane were oily liquids.

(E)-1-phenyl-2-(tri-n-butylgermyl)ethene (no. 1, Table 1)

Analytical data: ^{1}H NMR [$CDCl_3$; δ (ppm)]: 0.85–0.96 (m, 15H, CH_3 and CH_2), 1.27–1.44 (m, 12H, CH_2), 6.64 (d, 1H, J_{H-H} = 19.2 Hz, $Ge{-}HC{=}CH$), 6.82 (d, 1H, J_{H-H} = 19.2 Hz, $Ge{-}HC{=}CH$), 7.25 (d, 1H, J_{H-H} = 7.2 Hz, $p\text{-}C_6H_5$), 7.34 (t, 2H, $m\text{-}C_6H_5$), 7.44 (d, 2H, J_{H-H} = 6.6 Hz, $o\text{-}C_6H_5$). ^{13}C NMR [$CDCl_3$; δ (ppm)]: 13.06 (CH_2), 13.90 (CH_3), 26.60 (CH_2), 27.51 (CH_2), 126.05 ($o\text{-}C_6H_5$), 127.45 ($Ge{-}HC{=}CH$), 128.37 ($m\text{-}C_6H_5$), 128.90 ($p\text{-}C_6H_5$), 138.38 ($c_i\text{-}C_6H_5$), 142.76 ($Ge{-}HC{=}CH$). MS (EI) [m/z (rel. int., %)] = 337 ($M^{+\cdot}$, 23), 291 ($M^{+\cdot} - CH_2CH_2CH_2CH_3$, 100), 232 (20), 177 (18), 103 (5), 55 (6). Elemental analysis calcd (%) for $C_{20}H_{34}Ge$: C 69.20, H 9.87; found: C 69.26, H 9.94. Isolated yield 84%.

(E)-9-[2-(tri-n-butylgermyl)ethenyl]-9H-carbazole (no. 3, Table 1)

Analytical data: ^{1}H NMR [$CDCl_3$; δ (ppm)]: 0.85–0.99 (m, 15H, CH_3 and CH_2), 1.27–1.54 (m, 12H, CH_2), 6.14 (d, 1H, J_{H-H} = 17.1 Hz, $Ge{-}HC{=}CH$), 7.20 (d, 1H, J_{H-H} = 17.1 Hz, $HC{=}CH{-}N$), 7.30 (t, 2H, J_{H-H} = 6.9 Hz, $=CH$), 7.49 (t, 2H, J_{H-H} = 7.1 Hz, $=CH$), 7.68 (d, 2H, J_{H-H} = 8.2 Hz, $=CH$), 8.09 (d, 2H, J_{H-H} = 7.7 Hz, $=CH$). ^{13}C NMR [$CDCl_3$; δ (ppm)]: 13.18 (CH_2), 13.81 (CH_3), 26.48 (CH_2), 27.49 (CH_2), 110.47 ($=CH$), 114.06 ($Ge{-}CH{=}CH$), 120.21 ($=CH$), 120.40 ($=CH$), 123.82 (c_i), 126.09 ($=CH$), 132.33 ($CH{=}CH{-}N$), 139.29 (c_i). MS (EI) [m/z (rel. int., %)] = 380 ($M^{+\cdot} - CH_2CH_2CH_2CH_3$, 54), 324 (89), 268 (100), 240 (15), 205 (10), 55 (6). Elemental analysis calcd (%) for $C_{26}H_{37}GeN$: C 71.59, H 8.55, N 3.21; found: C 71.52, H 8.51, N 3.19. Isolated yield 63%.

(E)-1-(tri-n-butylgermyl)-2-(1′,3′-dioxolanyl)ethene (no. 5, Table 1)

Analytical data: ^{1}H NMR [$CDCl_3$; δ (ppm)]: 0.68–0.90 (m, 15H, CH_3 and CH_2), 1.27–1.39 (m, 12H, CH_2), 3.85–4.01 (m, 4H, $O{-}CH_2$), 5.18 (d, 1H, J_{H-H} = 5.7 Hz, $O{-}CH$), 5.91 (dd, 1H, J_{H-H} = 5.7 Hz, J_{H-H} = 18.6 Hz $Ge{-}CH{=}CH$), 6.30 (d, 1H, J_{H-H} = 18.4 Hz, $Ge{-}CH{=}CH$). ^{13}C NMR [$CDCl_3$; δ (ppm)]: 12.65 (CH_2), 13.71 (CH_3), 26.43 (CH_2), 27.25 (CH_2), 64.91 ($O{-}CH_2$), 105.13 ($O{-}CH$, from E/Z isomers), 136.12 ($Ge{-}CH{=}CH$), 140 ($Ge{-}CH{=}CH$). MS (EI) [m/z (rel. int., %)] = 287 ($M^{+\cdot} - CH_2CH_2CH_2CH_3$, 100), 245 (25), 231 (21), 189 (35), 173 (18), 131 (60), 100 (21), 74 (99), 45 (70). Elemental analysis calcd (%) for $C_{17}H_{34}GeO_2$: C 59.51, H 9.99; found: C 59.47, H 9.92. Isolated yield 85%.

(E/Z)-1-(butoxy)-2-(tri-n-butylgermyl)ethene (no. 6, Table 1)

Analytical data: (**a,b**) ^{1}H NMR [$CDCl_3$; δ (ppm)]: 0.72–0.97 (m, 14H, $Ge{-}CH_2$ and CH_3 from E/Z isomers), 1.26–1.38 (m, 12H $Ge{-}CH_2{-}CH_2{-}CH_2$, from E/Z isomers), 1.40–1.66 (m, 4H, $O{-}CH_2{-}CH_2{-}CH_2{-}CH_3$, from E/Z isomers), 3.70 (t, 2H, J_{H-H} = 6.59 Hz, $O{-}CH_2$ from E isomer), 3.71 (t, 2H, J_{H-H} = 6.32 Hz, $O{-}CH_2$ from Z isomer), 4.25 (d, 1H, J_{H-H} = 7.5 Hz, $Ge{-}HC{=}CH$, from Z isomer), 4.54 (d, 1H, J_{H-H} = 15.3 Hz, $Ge{-}HC{=}CH$, from E isomer), 6.26 (d, 1H, J_{H-H} = 15.0 Hz, $HC{=}CH{-}O$, from E isomer), 6.63 (d, 1H, J_{H-H} = 7.8 Hz, $HC{=}CH{-}O$, from Z isomer). ^{13}C NMR [$CDCl_3$; δ (ppm)]: 13.44 ($Ge{-}CH_2$, from Z isomer), 13.93 ($Ge{-}CH_2$, from E

isomer), 13.89 (Ge–CH$_2$–*CH*$_3$, from *E* isomer), 13.89 (Ge–CH$_2$–*CH*$_3$, from *Z* isomer), 19.19 (CH$_3$–*CH*$_2$, from *Z* isomer), 19.36 (CH$_3$–*CH*$_2$, from *E* isomer), 26.58 (Ge–CH$_2$–CH$_2$–*CH*$_2$, from *Z* isomer), 26.65 (Ge–CH$_2$–CH$_2$–*CH*$_2$, from *E* isomer), 27.44 (Ge–CH$_2$–*CH*$_2$–CH$_2$, from *E* isomer), 27.66 (Ge–CH$_2$–*CH*$_2$–CH$_2$, from *Z* isomer), 31.35 (O–CH$_2$–*CH*$_2$, from *E* isomer), 32.05 (O–CH$_2$–*CH*$_2$, from *Z* isomer), 67.47 (O–CH$_2$–CH$_2$, from *E* isomer), 71.50 (O–CH$_2$–CH$_2$, from *Z* isomer), 93.30 (GeCH=CH, from *E* isomer), 97.96 (GeCH=CH, from *Z* isomer), 153.69 (CH=*CH*–O, from *E* isomer), 156.41 (CH=*CH*–O, from *Z* isomer). MS (EI) [*m/z* (rel. int., %)] for (a) = 287 (M$^{+\cdot}$ − CH$_2$CH$_2$CH$_2$CH$_3$, 100), 262 (9), 244 (5), 228 (17), 185 (8), 171 (13), 131 (15), 115 (6), 103 (8), 89 (6), 56 (8). MS (EI) [*m/z* (rel. int., %)]for (b) = 287 (M$^{+\cdot}$ − CH$_2$CH$_2$CH$_2$CH$_3$, 100), 262 (12), 229 (41), 185 (11), 171 (20), 131 (21), 115 (8), 103 (10), 89 (14), 56 (16). Elemental analysis calcd (%) for $C_{18}H_{38}GeO$: C 63.01, H 11.16; found: C 63.09, H 11.12. Isolated yield 89%.

Representative procedure for the synthesis of [R$_3$Ge–CH=CH–R′], as well as [Et$_3$Ge–CH=CH–R–CH=CH$_2$] and [Et$_3$Ge–CH=CH–R–CH=CH–GeEt$_3$]

In a typical test, the ruthenium catalyst [RuH(Cl)(CO)(PCy$_3$)$_2$)] (2 mol%) was dissolved in toluene and placed in a glass ampoule under argon. Then the reagents and decane as an internal standard (5% by volume all components), vinylgermane and olefin or diene {usually used at the molar ratio $[\mathrm{Ru}]:[\mathrm{R_3GeCH{=}CH_2}]:[\mathrm{R'CH{=}CH_2}] = 2 \times 10^{-2}:1:3$ or $2 \times 10^{-2}:1:10$, for vinylsilanes $[\mathrm{Ru}]:[\mathrm{R_3GeCH{=}CH_2}]:[\mathrm{R'_3SiCH{=}CH_2}] = 2 \times 10^{-2}:1:5$ or $2 \times 10^{-2}:1:10$ and for dienes $[\mathrm{Ru}]:[\mathrm{Et_3GeCH{=}CH_2}]:[\mathrm{R'(CH{=}CH_2)_2}] = 2\times10^{-2}:6:1$} were added. Then, the ampoule was heated from 80 to 120 °C and maintained at that temperature for 24 h (48 h for dienes). The final products were separated from the residues of the catalyst and reagents by using a column with silica. The progress of the reaction was controlled by GC and GCMS. All products of the catalytic transformation of olefins and dienes with vinylgermanes were oily liquids.

(E)-4-[(triethylgermyl)ethenyl]-1-cyclohexene-1,2-epoxide (no. 11, Table 2)

Analytical data: ^{1}H NMR [CDCl$_3$; δ (ppm)]: 0.82 (q, 6H, $J_{\mathrm{H-H}} = 8.1$ Hz, *CH*$_2$), 1.01 (t, 9H, $J_{\mathrm{H-H}} = 8.1$ Hz, *CH*$_3$), 3.96 (m, 7H, *CH* and *CH*$_2$), 5.18 [dd, 2H, $J_{\mathrm{H-H}} = 5.8$ Hz, (*CH*–*CH*)O], 5.93 (dd, 1H, $J_{\mathrm{H-H}} = 5.8$ Hz, $J_{\mathrm{H-H}} = 18.5$ Hz, Ge–HC=*CH*–), 6.30 (d, 1H, $J_{\mathrm{H-H}} = 18.0$ Hz, Ge–*HC*=CH). ^{13}C NMR [CDCl$_3$; δ (ppm)]: 4.25 (CH$_2$), 8.96 (CH$_3$), 29.78 (CH$_2$), 64.96 (CH$_2$), 105.06 (CH), 134.90 (Ge–CH=CH), 140.47 (Ge–CH=CH). MS (EI) [*m/z* (%)] = 255 (M$^{+\cdot}$ − CH$_3$CH$_2$, 100), 238 (6), 225 (22), 205 (6), 179 (10), 157 (12), 133 (36), 105 (43), 91(18), 79(34), 56 (7). Elemental analysis calcd (%) for $C_{14}H_{26}GeO$: C 59.42, H 9.26; found: C 59.50, H 9.31. Isolated yield 59%.

(E)-1-(triethylgermyl)-2-(trimethylsilyl)ethene (no. 14, Table 2)

Analytical data: ^{1}H NMR [CDCl$_3$; δ (ppm)]: 0.06 (s, 9H, Si–*CH*$_3$) 0.79 (q, 6H, $J_{\mathrm{H-H}} = 8.1$ Hz, *CH*$_2$), 1.00 (t, 9H, $J_{\mathrm{H-H}} = 8.1$ Hz, *CH*$_3$), 6.49 (d, 1H, $J_{\mathrm{H-H}} = 21.9$ Hz,, Ge–*HC*=CH), 6.67 (d, 1H, $J_{\mathrm{H-H}} = 22.2$ Hz, Ge–HC=*CH*). ^{13}C NMR [CDCl$_3$; δ (ppm)]: −1.33 (Si–CH$_3$), 4.18 (CH$_2$), 9.03 (CH$_3$), 147.51 (Ge–HC=CH), 150.52 (Ge–HC=CH). ^{29}Si NMR [CDCl$_3$; δ (ppm)]: 7.93 (*Si*CH$_3$). MS(EI) [*m/z* (rel. int., %)] = 259 (M$^{+\cdot}$, 2), 243 (M$^{+\cdot}$ − CH$_3$, 7), 231 (M$^{+\cdot}$ − CH$_2$CH$_3$, 100), 217 (5), 203 (23), 173 (10), 161 (9), 147 (9), 133 (42), 119 (7), 103 (29), 83 (6), 73 (36) 59 (7). Elemental analysis calcd (%) for $C_{11}H_{26}GeSi$: C 51.00, H 10.12; found: C 51.06, H 10.08. Isolated yield 51%.

(E)-1-(triethylgermyl)-2-(triethoxysilyl)ethene (no. 17, Table 2)

Analytical data: ^{1}H NMR [CDCl$_3$; δ (ppm)]: 0.80 (q, 6H, $J_{\mathrm{H-H}} = 8.1$ Hz, *CH*$_2$), 1.00 (t, 9H, $J_{\mathrm{H-H}} = 8.1$ Hz, *CH*$_3$), 1.23 (t, 9H, $J_{\mathrm{H-H}} = 7.0$ Hz, OCH$_2$*CH*$_3$), 3.82 (q, 6H, $J_{\mathrm{H-H}} = 6.9$ Hz, O*CH*$_2$CH$_3$), 6.25 (d, 1H, $J_{\mathrm{H-H}} = 22.5$ Hz, Ge–*HC*=CH), 7.10 (d, 1H, $J_{\mathrm{H-H}} = 22.5$ Hz, Ge–HC=*CH*). ^{13}C NMR [CDCl$_3$; δ (ppm)]: 4.08 (CH$_2$), 8.98 (–CH$_3$), 18.31 (OCH$_2$CH$_3$), 58.52 (OCH$_2$CH$_3$), 138.71 (Ge–HC=CH), 156.08 (Ge–HC=CH). ^{29}Si NMR [CDCl$_3$; δ (ppm)]: −19.11 (*Si*OCH$_2$CH$_3$). MS(EI) [*m/z* (rel. int., %)] = 349 (M$^{+\cdot}$, 2), 321 (M$^{+\cdot}$ − CH$_2$CH$_3$, 100), 292 (20), 277 (19), 250 (5), 187 (8), 163 (17), 133 (15), 119 (15), 103 (21), 63 (14). Elemental analysis calcd (%) for $C_{14}H_{38}GeO_3Si$: C 48.16, H 9.24; found: C 48.22, H 9.29. Isolated yield 45%.

(E/Z)-1-butoxy-2-phenyldimethylgermylethene (no. 19, Table 2)

Analytical data: ^{1}H NMR [CDCl$_3$; δ (ppm)]: 0.45 (s, 6H, Ge–*CH*$_3$, for *E*), 0.49 (s, 6H, Ge–*CH*$_3$, for *Z*), 0.91 (t, 3H, $J_{\mathrm{H-H}} = 7.4$ Hz, *CH*$_3$, for *E*), 0.94 (t, 3H, $J_{\mathrm{H-H}} = 7.4$ Hz, *CH*$_3$, for *Z*), 1.26–1.45 (m, 4H, *CH*$_2$, for *E*/*Z*), 1.49–1.69 (m, 4H, *CH*$_2$ for *E*/*Z*), 3.74 (t, 2H, $J_{\mathrm{H-H}} = 6.3$ Hz, O–*CH*$_2$ for *Z*), 3.76 (t, 2H, $J_{\mathrm{H-H}} = 6.3$ Hz, O–*CH*$_2$ for *E*), 4.46 (d, 1H, $J_{\mathrm{H-H}} = 7.2$ Hz, Ge–*HC*=CH, for *Z*), 4.73 (d, 1H, $J_{\mathrm{H-H}} = 15.0$ Hz, Ge–*HC*=CH, for *E*), 6.37 (d, 1H, $J_{\mathrm{H-H}} = 15.0$ Hz, HC=*CH*–O, for *E*), 6.71 (d, 1H, $J_{\mathrm{H-H}} = 7.5$ Hz, HC=*CH*–O, for *Z*), 7.43 (m, 10H, C$_6$H$_5$ for *E*/*Z*). ^{13}C NMR [CDCl$_3$; δ (ppm)]: −2.28 (Ge–CH$_3$, for *E*), −1.59(Ge–CH$_3$, for *Z*), 13.86 (CH$_3$, for *E*), 13.95 (CH$_3$, for *Z*), 19.10 (CH$_2$, for *E*), 19.34 (CH$_2$, for *Z*), 31.28 (O–CH$_2$–CH$_2$, for *Z*), 31.98 (O–CH$_2$–CH$_2$, for *E*), 67.69 (O–CH$_2$–CH$_2$, for *Z*), 71.81 (O–CH$_2$–CH$_2$, for *E*), 94.16 (Ge–CH=CH, for *Z*), 98.66 (Ge–CH=CH, for *E*), 127.68 (*m*-C$_6$H$_5$ for *Z*), 127.78 (*m*-C$_6$H$_5$ for *E*), 127.85 (*p*-C$_6$H$_5$ for *E*), 127.95 (*p*-C$_6$H$_5$ for *Z*), 133.15 (*o*-C$_6$H$_5$ for *E*), 133.18 (*o*-C$_6$H$_5$ for *Z*), 141.36 (*c$_i$*-C$_6$H$_5$, for *Z*), 142.26 (*c$_i$*-C$_6$H$_5$, for *E*), 155.00 (CH=CH–O, for *Z*), 157.22 (CH=CH–O, for *E*). MS (EI) [*m/z* (%)] for *Z* = 265 (M$^{+\cdot}$ − CH$_3$, 45), 239 (80), 208 (22), 193 (11), 181 (21), 167 (100), 151 (16), 133 (9), 120 (13), 103 (19), 91 (37), 78 (22), 51 (23). MS (EI) [*m/z* (%)] for *E* = 265 (M$^{+\cdot}$ − CH$_3$, 52), 239 (75), 206 (18), 193 (9), 181 (23), 167 (100), 151 (20), 133 (8), 120 (10), 103 (16), 91 (37), 78 (20), 51 (22). Elemental analysis calcd (%) for $C_{14}H_{22}GeO$: C 60.28, H 7.95; found: C 60.33, H 7.93. Isolated yield 45%.

(E/Z)-1-(phenyldimethylgermyl)-2-(1′,3′-dioxolanyl)ethene (no. 20, Table 2)

Analytical data: ^{1}H NMR [CDCl$_3$; δ (ppm)]: 0.48 (s, 6H, *CH*$_3$), 3.86–4.04 (m, 4H, O–*CH*$_2$), 4.24 (d, 2H, $J_{\mathrm{H-H}} = 4.1$ Hz, O–*CH*), 5.22 (d, 2H, 1H, $J_{\mathrm{H-H}} = 5.7$ Hz, Ge–*CH*=CH, for *E* and *Z*), 6.00 (d, 1H, $J_{\mathrm{H-H}} = 5.7$ Hz, Ge–CH=*CH*, for *Z*), 6.40 (dd, 1H, $J_{\mathrm{H-H}} = 18.3$ Hz, Ge–CH=*CH* for *E*), 7.36 (t, 1H, $J_{\mathrm{H-H}} = 8.6$ Hz, *p*-C$_6$*H*$_5$), 7.45 (t, 2H, *m*-C$_6$*H*$_5$), 7.61 (d, 2H, $J_{\mathrm{H-H}} = 18.6$ Hz, *o*-C$_6$*H*$_5$). ^{13}C NMR [CDCl$_3$; δ (ppm)]: −3.41(CH$_3$), 65.00 (CH$_2$), 104.72 (O–CH), 128.05–151.03 (CH). MS (EI) [*m/z* (%)] for *E* = 279 (M$^{+\cdot}$, 2), 265 (M$^{+\cdot}$ − CH$_3$, 13), 235 (5), 221 (8), 203 (5), 193 (7), 181 (10), 165 (7), 149 (17), 131 (8), 115 (10), 99 (100), 89 (11), 73 (40), 55 (23), 45 (32). MS (EI) [*m/z* (%)] for *Z* = 279 (M$^{+\cdot}$, 2), 265 (M$^{+\cdot}$ − CH$_3$, 22), 238 (7), 221 (7), 203 (42), 187 (19), 175 (18), 149 (47), 131 (29), 115 (28), 99 (100), 89 (45), 73 (62), 51 (29), 45 (67). Elemental analysis calcd (%) for $C_{13}H_{18}GeO_2$: C 55.98, H 6.50; found: C 56.04, H 6.54. Isolated yield 60%.

4-[2-(Triethylgermyl)ethenyl]1-vinylbenzene and 1,4-bis[2-(triethyl germyl)ethenyl]benzene (no. 22, Table 2)

Analytical data: (c) ^{1}H NMR [CDCl$_3$; δ (ppm)]: 0.88 (q, 6H, $J_{\mathrm{H-H}} = 8.1$ Hz, *CH*$_2$), 1.07 (t, 9H, $J_{\mathrm{H-H}} = 8.1$ Hz, *CH*$_3$), 5.24

(d, 1H, $J_{\mathrm{H-H}}$ = 9.9 Hz, HC=CH_2), 5.75 (d, 1H, $J_{\mathrm{H-H}}$ = 17.6 Hz, HC=CH_2), 6.62 (d, 1H, $J_{\mathrm{H-H}}$ = 18.9 Hz, Ge–HC=CH), 6.69 (t, 1H, HC=CH$_2$), 6.82 (d, 1H, $J_{\mathrm{H-H}}$ = 18.9 Hz, Ge–HC=CH), 7.38 (s, 2H, $\mathrm{C_6}H_4$), 7.39 (s, 2H, $\mathrm{C_6}H_4$). ^{13}C NMR [CDCl$_3$; δ (ppm)]: 4.40 (CH$_2$), 8.95 (CH$_3$), 113.57 (CH=CH$_2$), 126.28 (Ge–HC=CH), 127.72 (C_6H$_4$), 127.93 (C_6H$_4$), 136.51 (CH=CH$_2$), 136.85 (c_i-C_6H$_4$), 137.91 (c_i-C_6H$_4$), 142.92 (Ge–HC=CH). MS (EI) [m/z (rel. int., %)] = 290 (M$^{+\cdot}$, 5), 260 (M$^{+\cdot}$ − CH$_2$CH$_3$, 100), 229 (22), 201 (26), 175 (13), 151 (5), 128 (20), 115 (8), 102 (18), 75(17), 52 (9). Elemental analysis calcd (%) for $\mathrm{C_{16}H_{24}Ge}$: C 66.49, H 8.37; found: C 66.45, H 8.40. Isolated yield 31%. (d) ^{1}H NMR [CDCl$_3$; δ (ppm)]: 0.86 (q, 12H, $J_{\mathrm{H-H}}$ = 8,1 Hz, CH_2), 1.06 (t, 18H, $J_{\mathrm{H-H}}$ = 8,1 Hz, CH_3), 6.60 (d, 2H, $J_{\mathrm{H-H}}$ = 18,9 Hz, Ge–HC=CH), 6.80 (d, 2H, $J_{\mathrm{H-H}}$ = 18.9 Hz, Ge–HC=CH), 7.38 (s, 4H, $\mathrm{C_6}H_4$). ^{13}C NMR [CDCl$_3$; δ (ppm)]: 4.40 (CH$_2$), 8.95 (CH$_3$), 126.29 (C_6H$_4$), 126.36 (Ge–HC=CH), 137.70 (c_i-C_6H$_4$), 142.92 (Ge–HC=CH). MS (EI) [m/z (rel. int., %)] = 419 (M$^{+\cdot}$ − CH$_2$CH$_3$, 100), 260 (7), 229 (17), 201 (15), 159 (93), 131 (71), 103 (41), 73(36), 56 (6). Elemental analysis calcd (%) for $\mathrm{C_{22}H_{38}Ge_2}$: C 59.01, H 8.55; found: C 59.08, H 8.60. Isolated yield 44%.

3,9-bis[2′-(Triethylgermyl)ethenyl]-2,4,8,10-tetraoxaspiro[5.5]undecane (no. 23, Table 2)

Analytical data: ^{1}H NMR [CDCl$_3$; δ (ppm)]: 0.80 (q, 12H, $J_{\mathrm{H-H}}$ = 8.1 Hz, CH_2), 1.01 (t, 18H, $J_{\mathrm{H-H}}$ = 8.1 Hz, CH_3), 3.42–3.68 (m, 8H, O–CH_2), 4.74 (t, 2H, $J_{\mathrm{H-H}}$ = 3.3 Hz, O–CH–O), 5.95 (dd, $J_{\mathrm{H-H}}$ = 10.2 Hz, Ge–HC=CH), 6.26 (d, 2H, $J_{\mathrm{H-H}}$ = 18.6 Hz, Ge–HC=CH). ^{13}C NMR [CDCl$_3$; δ (ppm)]: 4.23 (CH$_2$), 8.96 (CH$_3$), 32.48 (c_i), 70.21 (CH$_2$), 70.62 (CH$_2$), 101.94 (O–CH–O), 133.24 (Ge–HC=CH), 140.27 (Ge–HC=CH). MS (EI) [m/z (rel. int., %)] = 501 (M$^{+\cdot}$ − CH$_2$CH$_3$, 2), 303 (5), 255 (31), 187 (100), 157 (32), 131 (35), 103 (36), 70(40), 56 (59). Elemental analysis calcd (%) for $\mathrm{C_{23}H_{44}Ge_2O_4}$: C 52.13, H 8.37; found: C 52.08, H 8.40. Isolated yield 68%.

Procedure for synthesis of [Ph–CH= CH–GeEt$_2$–CH= CH$_2$] and [Ph–CH= CH–GeEt$_2$–CH= CH–Ph] [Ed. (3), a, b; Table 3]

[RuH(Cl)(CO)(PCy$_3$)$_2$] complex (42 mg, 0.058 mmol), toluene (4.25 ml), diethyldivinylgermane (0.532 g, 2.89 mmol) and styrene (1.806 g, 17.34 mmol) were placed in 15 ml glass ampoule. The ampoule was heated in the argon at 110 °C for 48 h. The final product was separated from residues of the catalyst and the remains of styrene and diethyldivinylgermane using column with silica. The progress of the reaction was controlled by GC and GCMS. Products of the catalytic transformation of styrene with diethyldivinylgermane were oily liquids.

(E)-2-phenyl-1-diethylvinylgermylethene and (E)-2,2-bisphenylethenyldiethylgermane [no. 24(a) and 25(b), Table 3]

Analytical data: (a) ^{1}H NMR [CDCl$_3$; δ (ppm)]: 0.96 (q, 4H, $J_{\mathrm{H-H}}$ = 8.1 Hz, CH_2), 1.09 (t, 6H, $J_{\mathrm{H-H}}$ = 8.1 Hz, CH_3), 5.67–6.10 (dd, 2H, $J_{\mathrm{H-H}}$ = 3.6 Hz, $J_{\mathrm{H-H}}$ = 20.1 Hz, GeCH=CH$_2$); 6.32 (dd, 4H, $J_{\mathrm{H-H}}$ = 13.7 Hz, $J_{\mathrm{H-H}}$ = 6.3 Hz, GeCH=CH_2), 6.61 (d, 1H, $J_{\mathrm{H-H}}$ = 18.9 Hz, GeCH=CH), 6.86 (d, 1H, $J_{\mathrm{H-H}}$ = 18.9 Hz, GeCH=CH), 7.24–7.46 (m, 5H, $\mathrm{C_6}H_5$). ^{13}C NMR [CDCl$_3$; δ (ppm)]: 5.35 (CH$_2$), 8.98 (CH$_3$), 126.12 (m-C_6H$_5$), 126.40 (p-C_6H$_5$), 127.68 (Ge–HC=CH), 128.39 (o-C_6H$_5$), 131.49 (GeCH=CH$_2$), 136.38 (GeCH=CH$_2$), 138.10 (c_i-C_6H$_5$), 143.94 (Ge–HC=CH). MS (EI) [m/z (rel. int., %)] = 262 (M$^{+\cdot}$, 9), 233 (M$^{+\cdot}$ − CH$_2$CH$_3$, 100), 205 (41), 177 (24), 151 (19), 129 (21), 115 (8), 101 (36), 77 (18), 52 (17). Elemental analysis calcd (%) for $\mathrm{C_{14}H_{20}Ge}$: C 64.44, H 7.73; found: C 64.50, H 7.76. Isolated yield 40%. (b) ^{1}H NMR [CDCl$_3$; δ (ppm)]: 1.05 (q, 4H, $J_{\mathrm{H-H}}$ = 8.1 Hz, CH_2), 1.12 (t, 6H, $J_{\mathrm{H-H}}$ = 8.1 Hz, CH_3), 6.67 (d, 1H, $J_{\mathrm{H-H}}$ = 18.9 Hz, GeCH=CH), 6.92 (d, 1H, $J_{\mathrm{H-H}}$ = 18.9 Hz, GeCH=CH), 7.25–7.47 (m, 5H, $\mathrm{C_6}H_5$). ^{13}C NMR [CDCl$_3$; δ (ppm)]: 5.71 (CH$_2$), 9.08 (CH$_3$), 126.16 (m-C_6H$_5$), 126.47 (p-C_6H$_5$), 127.73 (Ge–HC=CH), 128.42 (o-C_6H$_5$), 138.08 (c_i-C_6H$_5$), 144.11 (Ge–HC=CH). MS (EI) [m/z (rel. int., %)] = 338 (M$^{+\cdot}$, 7), 309 (M$^{+\cdot}$ − CH$_2$CH$_3$, 100), 281 (29), 251 (8), 235 (33), 206 (92), 177 (66), 151 (54), 128 (26), 117 (38), 103 (36), 91 (51), 77 (38), 52 (55). Elemental analysis calcd (%) for $\mathrm{C_{20}H_{24}Ge}$: C 71.27, H 7.18; found: C 71.33, H 7.23. Isolated yield 25%.

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