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Transition Metal-Catalyzed Dehydrogenative Germylation of Olefins with Tri-*n*-butylgermane

Naoyuki Furukawa, Noriko Kourogi, and Yoshio Seki*

Laboratory of Commodity Science, Faculty of Economics, Kagawa University, Takamatsu, Kagawa 760-8523, Japan

Fumitoshi Kakiuchi and Shinji Murai*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

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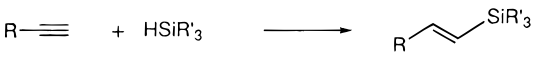
Summary: The catalyzed reaction of an excess of styrene with n-Bu$_3$GeH using several ruthenium and rhodium complexes gave the corresponding vinylgermanes (α-tri-n-butylgermylstyrene, (Z)-β-tri-n-butylgermylstyrene, and (E)-β-tri-n-butylgermylstyrene), which are dehydrogenative germylation products. The most effective catalyst was Ru$_3$(CO)$_{12}$, whose use resulted in selective formation of the vinylgermanes in high yields.

Introduction

It is well-known that metal-catalyzed reactions of hydrosilanes parallel those of hydrogermanes. For example, the catalyzed reaction of alkynes with a hydrosilane produces vinylsilanes as shown in eq 1.[1] Similarly, the reaction of alkynes with a hydrogermane gives vinylgermanes (eq 2).[2] Hydrosilylation of olefins with a hydrosilane is well-known to give alkylsilanes (eq 3).[1] Similarly, the reaction of olefins with a hydrogermane usually produces alkylgermanes (eq 4).[2]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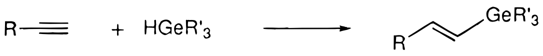
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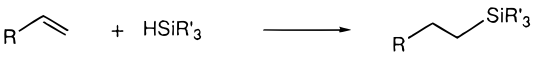
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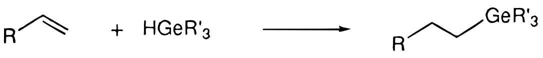
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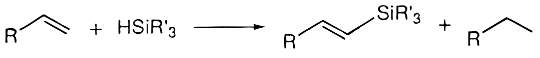
Although dehydrogenative silylation, which produces vinylsilanes directly from hydrosilanes and olefins (eq 5), is less common than the hydrosilylation of olefins, it has been extensively studied in the last two decades.[3] On the other hand, no example of dehydrogenative germylation, which would produce vinylgermanes directly from hydrogermanes and olefins, has been reported (eq 6).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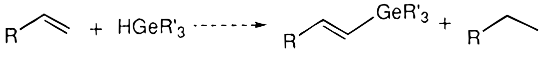
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Vinylsilanes are versatile synthetic intermediates in organic synthesis,[4] and the dehydrogenative silylation reaction provides a useful method for their preparation. Similarly, a new synthesis of vinylgermanes by the dehydrogenative germylation of olefins is expected to be a useful development in vinylgermane chemistry. Ru$_3$(CO)$_{12}$-catalyzed dehydrogenative silylation of olefins has already been reported as the first example of the exclusive formation of vinylsilanes from hydrosilanes and olefins.[3c,e] We have now found that Ru$_3$(CO)$_{12}$ also is an active catalyst for the dehydrogenative

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Table 1. Catalytic Activities of Ruthenium Metal Complexes[a]

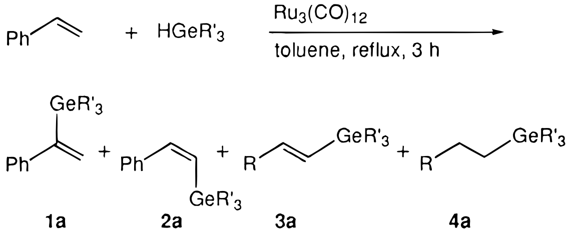
	yield, %			
	1a	**2a**	**3a**	**4a**
$Ru_3(CO)_{12}$	2	4	91	0
$RuHCl(CO)(PPh_3)_3$	0	1	62	6
$RuCl_2(PPh_3)_4$	0	1	20	1
$RuCl_2(PPh_3)_3$	0	0	10	2
$RuHCl(PPh_3)_3$	0	0	7	0
$[RuCl_2(benzene)]_2$	0	0	6	1
$RuH_2(PPh_3)_4$	0	0	3	0

[a] Reaction conditions: styrene (2.5 mmol), *n*-Bu_3GeH (0.25 mmol), catalyst (0.01 mmol), toluene (5 mL), reflux, 3 h.

germylation of olefins with hydrogermanes to give vinylgermanes selectively.

Results and Discussion

Dehydrogenative Germylation of Styrene Catalyzed by Ruthenium Complexes. Ruthenium carbonyl-catalyzed reaction of styrene with tri-*n*-butylgermane afforded four types of products, α-tri-*n*-butylgermylstyrene (**1a**), (*Z*)-*β*-tri-*n*-butylgermylstyrene (**2a**), (*E*)-*β*-tri-*n*-butylgermylstyrene (**3a**), and a simple addition compound (**4a**) as shown in eq 7.[5] Products **1a**, **2a**, and **3a** are dehydrogenative germylation products, and **4a** is a hydrogermylation product. We have investigated the catalytic activity of various commercially available ruthenium complexes for the reaction of an excess of styrene with tri-*n*-butylgermane at toluene reflux condition. Typically, a solution of styrene (2.5 mmol), *n*-Bu_3GeH (0.25 mmol), and $Ru_3(CO)_{12}$ (0.01 mmol) in toluene (5 mL) was stirred at reflux for 3 h. GLC analysis showed that the reaction mixture contained **3a** in 91% yield, along with small amounts of **2a** (4%) and **1a** (2%).



(7)

Various transition metal complexes which have been known to be effective for dehydrogenative silylation and are easily available have been examined for the catalytic activities. The ruthenium complexes examined were $[RuCl_2(benzene)]_2$, $RuCl_2(PPh_3)_4$, $RuCl_2(PPh_3)_3$, $RuH_2(PPh_3)_4$, $RuHCl(PPh_3)_3$, $RuHCl(CO)(PPh_3)_3$, $[RuCl_2(p\text{-}cymene)]_2$, $Ru(acac)_3$, $CpRuCl(PPh_3)_2$, $RuH_2(CO)(PPh_3)_3$, $RuCl_2(CO)_2(PPh_3)_2$, $[Cp^*RuCl_2]_n$, Cp^*_2Ru, Cp_2Ru, $[RuCl_2(CO)_3]_2$, $RuCl_3$, and $Ru_3(CO)_{12}$. Several ruthenium complexes that showed catalytic activity are listed in Table 1. The reaction using $Ru_3(CO)_{12}$ selectively gave the corresponding vinylgermanes in quantitative yield. We had already found that $Ru_3(CO)_{12}$ is the most effective catalyst for the dehydrogenative silylation of styrene.[3] The fact that dehydrogenative germylation has taken place implies that degermylation is involved in the reaction course, and this represents the first example, to the best of our knowledge, in the chemistry of germanium. This result suggests that the dehydrogenative silylation (eq 5) also parallels the dehydrogenative germylation (eq 6).

Table 2. Effect of the Reaction Conditions to the Yield

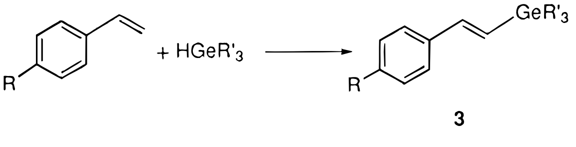
expt	styrene (mmol)	$HGeBu_3$ (mmol)	temp (°C)	time (h)	solvent	yield, %			
						1a	**2a**	**3a**	**4a**
1	2.5	0.25	reflux	3	toluene	2	4	91	0
2	1	0.25	reflux	3	toluene	2	0	66	0
3	0.5	0.25	reflux	3	toluene	1	1	53	0
4	0.25	0.25	reflux	3	toluene	0	1	31	0
5	0.1	0.25	reflux	3	toluene	0	1	43	1
6	2.5	0.25	100	3	toluene	0	0	34	0
7	2.5	0.25	80	3	toluene	0	0	2	0
8	2.5	0.25	110[a]	3	hexane	1	1	31	1
9	2.5	0.25	110[a]	22	hexane	1	2	70	1
10	2.5	0.25	100[a]	3	CH_3CN	0	0	39	0
11	2.5	0.25	100[a]	3	THF	0	0	0	0
12	2.5	0.25	60[a]	3	CH_2Cl_2	0	0	0	0

[a] Temperature of oil bath.

The effect of reaction conditions on the yield and the product distribution was examined in the $Ru_3(CO)_{12}$-catalyzed reaction of styrene with tri-*n*-butylgermane. No reaction occurred at 80 °C (expt 7 in Table 2). Using more vigorous reaction conditions such as toluene reflux, the correponding vinylgermane was obtained in high yield. In comparison, the similar reaction of a hydrosilane usually proceeds smoothly at 80 °C to give the vinylsilane in high yield.

The hydrogenation of styrene was a side-reaction to give ethylbenzene as a byproduct. A reaction using a 1:1 ratio of styrene to tri-*n*-butylgermane gave the vinylgermane in only 32% yield. The yield of the vinylgermane increased with an increase in the molar ratio of styrene to the hydrogermane, and with a 10-fold excess of styrene, the vinylgermane (**3a**) was obtained in high yield. Using hexane and acetonitrile as a solvent also gave the vinylgermane (**3a**) in 70% and 39% yields, respectively. On the other hand, no reaction occurred in THF and CH_2Cl_2.

Scope and Limitation with Respect to Olefins. Styrene derivatives smoothly reacted with hydrogermanes to give vinylgermanes (**3**), as shown in eq 8. The reaction of *p*-methylstyrene, *p*-chlorostyrene, *p*-fluorostyrene, and *p*-trifluoromethylstyrene also gave the corresponding vinylgermanes (**3c**, **3d**, **3e**, and **3f**) in 65%, 66%, 60%, and 56% yield, respectively. Triethylgermane also reacted smoothly to give **3b** in 58% yield.



(8)

The dehydrogenative silylation of allylbenzene and 1-hexene using $Ru_3(CO)_{12}$ is known to give the corresponding vinylsilane or allylsilane in high yield.[3c] The vinylsilane is obtained under mild reaction conditions, but the allylsilane requires vigorous conditions. On the other hand, the same reaction in which tri-*n*-butylger-

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(5) The products **1a**, **2a**, and **4a** were identified by agreement with the retention times and mass spectra of authentic samples. The authentic samples of **1a** and **2a** were prepared from phenylacetylene and *n*-Bu_3GeH. See ref 2c. That of **4a** was prepared by the $Ru(acac)(CO)_2$-catalyzed reaction of styrene with *n*-Bu_3GeH. The structure of **4a** was determined by NMR and IR spectra: ^1H NMR ($CDCl_3$) δ 0.60−1.84 (c, 29H, CH_2, Bu), 2.53−2.70 (m, 2H, CH_2), 7.16−7.36 (m, 5H, Ph); IR (neat) 2940 s, 2910 s, 2840 s, 1460 m, 1080 w, 700 m.

Table 3. Catalytic Activities of Rhodium Metal Complexes[a]

	yield, %			
	1a	**2a**	**3a**	**4a**
$Rh_6(CO)_{16}$	0	55	0	31
$RhH(CO)(PPh_3)_3$	0	0	13	67
$RhCl_3$	0	34	15	27
$[RhCl(CO)_2]_2$	0	0	32	30
[RhCl(1,5-hexadiene)]$_2$	0	36	0	25
$Rh_4(CO)_{12}$	0	30	0	30
$[Cp^*RhCl_2]_2$	0	0	47	10
$RhCl(CO)(PPh_3)_2$	0	0	34	21
[RhCl(COD)]$_2$	0	0	27	28
Rh(acac)$(CH_2{=}CH_2)_2$	0	0	30	17
$Cp^*Rh(CO)_2$	0	13	8	18

[a] Reaction conditions: styrene (2.5 mmol), *n*-Bu_3GeH (0.25 mmol), catalyst (0.01 mmol), toluene (5 mL), reflux.

mane was used did not give the vinylgermane and the allylgermane, respectively. To clarify the reason for this difference, product formation in the reaction of allylbenzene was examined with time. Allylbenzene was isomerized in the presence of $Ru_3(CO)_{12}$ to β-methylstyrene in the initial stages of the reaction. Internal olefins are less reactive than terminal olefins in dehydrogenative silylation.[3c] The same appears to be true for dehydrogenative germylation. The isomerization of allylbenzene to unreactive β-methylstyrene in the initial stage converted it to an unreactive internal olefin.

Dehydrogenative Germylation Catalyzed by Rhodium Complexes. The catalytic activity of many commercially available rhodium complexes was examined in the reaction of styrene with tri-*n*-butylgermane. The products obtained were the same as those in the $Ru_3(CO)_{12}$-catalyzed reaction. The rhodium complexes were $[RhCl(CO)_2]_2$, $RhCl(CO)(PPh_3)_2$, $RhH(CO)(PPh_3)_3$, Rh(acac)$(CH_2{=}CH_2)_2$, $Cp^*Rh(CO)_2$, $[Cp^*RhCl_2]_2$, $RhCl_3$, $Rh_6(CO)_{16}$, [RhCl(COD)]$_2$, $Rh_4(CO)_{12}$, [RhCl(1,5-hexadiene)]$_2$, $Rh(NO)(PPh_3)_3$, Rh(acac)$_3$, Rh(COD)$_2SO_3CF_3$, $[Rh(OAc)_2]_2$, $[Rh(OOCCF_3)_2]_2$, [RhCl(norbornadiene)]$_2$, $[RhCl(CH_2{=}CH_2)_2]_2$, [RhCl(cyclooctene)$_2$]$_2$, Rh(acac)(norbornadiene), [RhCl(2-phenylpyridine)$_2$]$_2$, $RhCl(PPh_3)_3$, and Rh(acac)(COD). Several of these rhodium complexes showed catalytic activity as shown in Table 3. In the all of these reactions, the simple hydrogermylation product (**4a**) also was produced. Some rhodium complexes gave the (*Z*)-isomer (**2a**) as main product. Recently, it was reported that rhodium complexes are active catalysts for the dehydrogenative silylation of olefins with a hydrosilane.[6] However, no example of the selective dehydrogenative silylation of olefins catalyzed by a rhodium complex has been reported. The fact that similar results were obtained with hydrosilanes and hydrogermanes suggests that the mechanisms of dehydrogenative silylation and germylation of olefins are very similar.

In conclution, this note reports the first example of the dehydrogenative germylation of olefins with a hydrogermane to give the vinylgermanes. This reaction provids a useful method of a vinylgermane.

Experimental Section

General Information. ^{1}H NMR spectra were recorded on a JEOL JMN-A400 spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity, coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a Shimadzu 435 spectrometer; absorptions are reported in cm^{-1}. Mass spectra were obtained on a Shimadzu GCMS-QP2000A with ionization voltage of 70 eV. Elemental analyses were performed by Elemental Analysis Section of Osaka University. Analytical GC was carried out on a Shimadzu GC-14A gas chromatograph, equipped with a flame ionization detector. Preparative GC was carried out on a Hitachi GC-164 gas chromatograph.

Materials. Toluene was distilled from CaH_2. $Ru_3(CO)_{12}$, *n*-Bu_3GeH, Et_3GeH, *p*-fluorostyrene, *p*-trifluoromethylstyrene were purchased from Aldrich Chemical Co. and used without further purification. *p*-Methylstyrene and *p*-chlorostyrene were purchased from Tokyo Kasei Kogyo Co. and used without further purification.

General Procedures. In a 10 mL, two-necked, round-bottomed flask were placed $Ru_3(CO)_{12}$ (0.01 mmol), *n*-Bu_3GeH (0.25 mmol), styrene (2.5 mmol), and toluene (5 mL). The reaction mixture was heated in an oil bath at reflux under an atmosphere of N_2. The reactions were complete within 3 h. The yields were determined by GLC, with *n*-heptadecane as internal standerd. The toluene was removed under reduced pressure, and the residue was passed through a short chromatography column of Wakogel C-200. Preparative GC afforded the analytical samples. The physical properties of new compounds are give below.

(*E*)-1-Phenyl-2-(tri-*n*-butylgermyl)ethylene (3a): Colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.82−0.92 (c, 15H, Bu), 1.30−1.43 (c, 12H, Bu), 6.62 (d, J = 18.9 Hz, 1H, CH=), 6.80 (d, J = 18.9 Hz, 1H, CH=), 7.22 (dd, J = 7.3, 7.3 Hz, 1H, Ph), 7.32 (dd, J = 7.3, 7.3 Hz, 1H, Ph), 7.42 (d, J = 7.3 Hz, 1H, Ph); IR (neat) 2910 s, 1599 m, 1572 w, 1495 m, 1460 m, 1418 w, 1377 m, 1341 w, 1292 w, 1192 w, 1078 w, 1022 w, 983 m, 878 w, 728 s, 687 m, 648 w; MS, *m/z* (rel intensity) 292 (54), 290 (41), 235 (74), 180 (88), 179 (100), 151 (51). Anal. Calcd for $C_{20}H_{34}Ge$: C, 69.21; H, 9.87. Found: C, 68.89; H,9.81.

(*E*)-1-(*p*-Methylphenyl)-2-(tri-*n*-butylgermyl)ethylene (3c): Colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.83−0.91 (c, 15H, Bu), 1.29−1.48 (c, 12H, Bu), 2.33 (s, 3H, CH_3), 6.55 (d, J = 19.0 Hz, 1H, CH=), 6.77 (d, J = 19.0 Hz, 1H, CH=), 7.13 (d, J = 8.0 Hz, 2H, Ph), 7.32 (d, J = 8.0 Hz, 2H, Ph); IR (neat) 2900 s, 1615 m, 1562 m, 1507 s, 1461 s, 1416 m, 1377 s, 1338 m, 1284 m, 1218 m, 1190 m, 1176 m, 1079 s, 1017 m, 980 s, 962 m, 905 m, 880 s, 834 m, 772 s, 733 s, 702 s, 648 m, 660 w; MS, *m/z* (rel intensity) 306 (52), 304 (37), 250 (61), 193 (100), 165 (48). Anal. Calcd for $C_{21}H_{36}Ge$: C, 69.85; H, 10.05. Found: C, 69.91; H, 10.05.

(*E*)-1-(*p*-Chlorophenyl)-2-(tri-*n*-butylgermyl)ethylene (3d): Colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.84−0.91 (c, 15H, Bu), 1.31−1.40 (c, 12H, Bu), 6.60 (d, J = 18.7 Hz, 1H, CH=), 6.74 (d, J = 18.7 Hz, 1H, CH=), 7.26−7.29 (m, 2H, Ph), 7.33−7.35 (m, 2H, Ph); IR (neat) 2943 s, 1599 m, 1487 s, 1459 m, 1401 m, 1376 m, 1338 w, 1269 w, 1094 m, 1011 m, 982 m, 879 w, 842 m, 778 s, 722 m, 698 m, 649 m; MS, *m/z* (rel intensity) 326 (39), 270 (67), 213 (100), 185 (33), 109 (29). Anal. Calcd for $C_{20}H_{33}Ge$: C, 62.96; H, 8.72 Found: C, 62.74; H, 8.72.

(*E*)-1-(*p*-Fluorophenyl)-2-(tri-*n*-butylgermyl)ethylene (3e): Colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.84−0.92 (c, 15H, Bu), 1.32−1.41 (c, 12H, Bu), 6.52 (d, J = 18.8 Hz, 1H, CH=), 6.75 (d, J = 18.8 Hz, 1H, CH=), 6.98−7.02 (m, 2H, Ph), 7.36−7.40 (m, 2H, Ph); IR (neat) 2944 s, 1599 m, 1487 s, 1459 m, 1400 m, 1376 m, 1093 m, 1011 m, 981 m, 841 m, 777 s, 693 m, 648 m; MS, *m/z* (rel intensity) 309 (39), 305 (22), 253 (57), 249 (32), 197 (100), 193 (67), 169 (41), 165 (24). Anal. Calcd for $C_{20}H_{33}Ge$: C, 65.80; H, 9.11 Found: C, 65.81; H, 8.91.

(*E*)-1-(*p*-Trifluoromethylphenyl)-2-(tri-*n*-butylgermyl)ethylene (3f): Colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.86−0.92 (c, 15H, Bu), 1.34−1.41 (c, 12H, Bu), 6.76 (d, J = 19.0 Hz, 1H, CH=), 6.83 (d, J = 19.0 Hz, 1H, CH=), 7.50 (d, J = 8.3 Hz,

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2H, Ph), 7.57 (d, $J = 8.3$ Hz, 2H, Ph); IR (neat) 2944 m, 1612 m, 1461 m, 1410 w, 1376 w, 1325 s, 1161 s, 1122 s, 1076 s, 1015 m, 982 m, 852 m, 788 m, 757 w, 707 w, 612 w; MS, *m*/*z* (rel intensity) 360 (24), 303 (72), 247 (100), 153 (85), 151 (68). Anal. Calcd for $C_{21}H_{33}F_3Ge$: C, 60.77; H, 8.01 Found: C, 60.82; H, 7.79.

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