One-Step Syntheses of Styryl Germatranes via Rhodium- or Palladium-Catalyzed Hydrogermylation of Arylacetylenes by $HGe(OCH_2CH_2)_3N$

J. W. Faller* and Roman G. Kultyshev

Department of Chemistry, Yale University, New Haven, Connecticut 06520

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Summary: *The addition of germatrane, $HGe(OCH_2CH_2)_3N$ (**1**), to terminal acetylenes is catalyzed by $[Cp^*RhCl_2]_2$ and yields styrylgermatranes The stereochemistry of the double bond can be controlled by the choice of solvent. In methylene chloride, (E)-β-styrylgermatranes are the major products, whereas in toluene (Z)-β-styrylgermatranes are the major products. The addition is also catalyzed by $Pd(PPh_3)_4$, giving (E)-β-styrylgermatranes regardless of solvent.*

Introduction

The transition metal-catalyzed addition of germanium hydrides to carbon−carbon multiple bonds is an efficient way to synthesize functionalized germanes. Previously, Oshima and co-workers[1] showed that in the presence of $Pd(PPh_3)_4$ triphenylgermane stereoselectively adds to terminal acetylenes, providing (*E*)-alkenyltriphenylgermanes in good yields. Hydrogermylation of isoprene by tri(2-furyl)germane in water in the presence of allylpalladium chloride dimer resulted in an allylic compound, (*E*)-β-methylcrotyltri(2-furyl)germane.[2]

Germatrane, $HGe(OCH_2CH_2)_3N$ (**1**), was first synthesized in 1981 by Mironov and co-workers.[3a] Although they investigated the possibility of using **1** for the preparation of other germatranes, in particular via its reactions with alkyl halides,[3b] to the best of our knowledge the addition of **1** to the triple bonds of alkynes has not been investigated. Our interest in the synthesis of alkenyl and styryl germatranes resulted from their potential application in palladium-catalyzed cross-coupling reactions and prompted us to explore **1** as a hydrogermylating reagent for alkynes.[4,5]

Results and Discussion

$[Cp^*RhCl_2]_2$- or $Pd(PPh_3)_4$-Catalyzed Hydrogermylation of Arylacetylenes. Recently our group reported the highly regio- and stereoselective hydrosilylation of phenylacetylene by triorganosilanes, $HSiR_3$ (R = Ph, Et, OEt), in the presence of catalytic amounts of $[Cp^*RhCl_2]_2$ (**2a**) that yielded (*Z*)-β-styrylsilanes.[4] Similarly, addition of germatrane **1** to phenylacetylene (**3a**) in dichloromethane in the presence of $[Cp^*RhCl_2]_2$ occurs in a highly regio- and stereoselective manner, but with the opposite stereochemistry (Table 1, entry 1). The ^{1}H NMR spectrum of the main product agrees with that reported by Lukevics and co-workers[6,7] for (*E*)-β-styrylgermatrane (*E*-**4a**) prepared by a different route. The rhodium-catalyzed hydrogermylation reactions of *p*-tolylacetylene (**3b**) and *p*-chlorophenylacetylene (**3c**) were less rapid than in the case of phenylacetylene; nevertheless, no germanium hydride remained after 3 days of stirring at room temperature (entries 2, 3). Small amounts of the corresponding stereoisomer *Z*-**4** and regioisomer **5** were also produced. The stereochemistry of (*E*)-β-(4-methyl)styrylgermatrane, *E*-**4b**, was confirmed by single-crystal X-ray diffraction analysis.

We observed that the stereochemical outcome of the rhodium-catalyzed addition of germatrane, **1**, to arylacetylenes, was solvent dependent. Thus, when instead of using CH_2Cl_2 as solvent, the reaction of **1** with phenylacetylene was performed in toluene under reflux, *Z*-**4a** was the major product (entry 4). The *cis*-stereochemistry was indicated by a smaller coupling between the olefinic protons (^3J = 14 Hz, whereas ^3J = 18 Hz for *E*-**4a**) and was confirmed by single-crystal X-ray diffraction. Similarly, hydrogermylation of 4-methyl and 4-chloro analogues, **3b** and **3c**, in toluene produced predominantly *Z*-**4b** and *Z*-**4c**, with *Z:E* ratios of 5.5:1 and 4.7:1, respectively (entries 5, 6). Traces of α-products **5b** and **5c** were also observed.

Having established that the stereochemical outcomes of the hydrogermylation reaction in dichloromethane and toluene were different, we investigated some other solvents. Addition of **1** to phenylacetylene in acetonitrile at room temperature was significantly slower than that in dichloromethane and resulted in only one-third conversion after the same reaction time, yet it also yielded predominantly the *trans*-styrylgermatrane, *E*-**4a**. Upon heating under reflux in acetonitrile **1** was completely consumed, yielding *E*-**4a** and the α-product, **5a**, in a ratio of 95:5. The latter was identified by a distinct AB pattern of its diastereotopic methylene protons at δ 5.97 and 5.90 ($CDCl_3$). Reaction in THF at room temperature was more sluggish (20% conversion) and less stereoselective, yielding both *E*- and *Z*-**4a**. Overnight reflux resulted in 42% conversion with an observed *Z*/*E* ratio of 1:1.4. Apparently, in toluene at reflux the reaction follows a pathway different from that in more polar solvents, such as dichloromethane and acetonitrile, whereas in THF, a solvent of an intermediate

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(2) Kinoshita, H.; Nakamura, T.; Kakiya, H.; Shinokubo, H.; Matsubara, S.; Oshima, K. *Org. Lett.* **2001**, *3*, 2521−2524.
(3) (a) Mironov, V. F.; Khromova, N. Yu.; Gar, T. K. *Zh. Obshch. Khim.* **1981**, *51*, 954−955. (b) Gar, T. K.; Khromova, N. Yu.; Tandura, S. N.; Mironov, V. F. *Zh. Obshch. Khim.* **1983**, *53*, 1800−1807.
(4) Faller, J. W.; D'Alliessi, D. G. *Organometallics* **2002**, *21*, 1743−1746.
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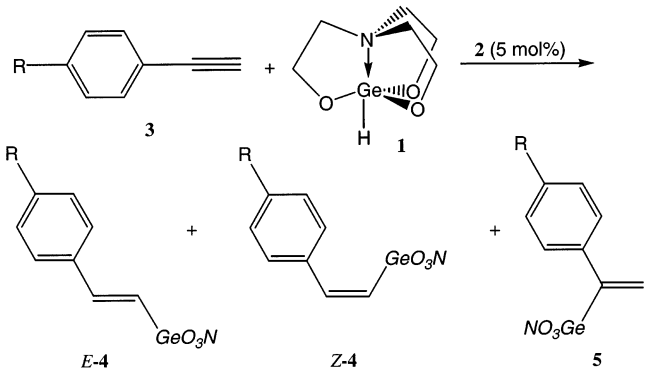
Table 1. Transition Metal-Catalyzed Hydrogermylation of Arylacetylenes by Germatrane, 1



entry	acetylene	R	catalyst[a]	reaction conditions	time, h[b]	*E*-**4**:*Z*-**4**:**5**[c]
1	**3a**	H	**2a**	CH_2Cl_2, r.t.	20	27.5:1.2:1
2	**3b**	CH_3	**2a**	CH_2Cl_2, r.t.	84	18.7:1.8:1
3	**3c**	Cl	**2a**	CH_2Cl_2, r.t.	70	22.9:1[d]
4	**3a**	H	**2a**	toluene, reflux	12	7.5:26.5:1
5	**3b**	CH_3	**2a**	toluene, reflux	12	5.4:29.7:1
6	**3c**	Cl	**2a**	toluene, reflux	12	6.2:29.4:1
7	**3a**	H	**2a**	acetonitrile, reflux	25	15.8:0[e]:1
8	**3a**	H	**2b**	THF, r.t.	51	62:2.3:1
9	**3a**	H	**2b**	toluene, reflux	18	*f*
10	**3b**	CH_3	**2b**	THF, r.t.	91	24.2:0[e]:1
11	**3c**	Cl	**2b**	THF, r.t.	48	12.6:0[e]:1

[a] **2a** = $[Cp^*RhCl_2]_2$; **2b** = $Pd(PPh_3)_4$. [b] Not optimized. [c] Determined by integration of olefinic protons in ^1H NMR spectra of crude products. [d] *E*-**4**:**5** ratio, signals of *Z*-**4** could not be integrated accurately. [e] Not observed by ^1H NMR. [f] Not determined.

polarity, both pathways are accessible.[8] Pure *E*-**4a** and *Z*-**4a** did not isomerize upon heating in toluene either in the presence or in the absence of $[Cp^*RhCl_2]_2$.

Initial attempts to use aliphatic alkynes such as 1-hexyne and trimethylsilylacetylene in the rhodium-catalyzed hydrogermylation reaction were not promising. In the former case only 20% conversion was achieved after 24 h of stirring in CH_2Cl_2. In the latter case no addition to the triple bond was observed after 25 h. Contrary to observations on related hydrosilylations,[4] $[Cp^*Rh(BINAP)](SbF_6)_2$ prepared in situ from [Cp*Rh(BINAP)Cl]Cl and $AgSbF_6$ did not catalyze the hydrogermylation of phenylacetylene by **1**.

The addition of germanium hydride **1** to aryl acetylenes proceeds also in the presence of $Pd(PPh_3)_4$ (**2b**). Although the palladium-catalyzed hydrogermylation of **3a** in THF is faster than in CH_2Cl_2, it is still slower than the corresponding rhodium-catalyzed reaction. The addition products were contaminated with triphenylphosphine oxide (TPPO) resulting from oxidation of triphenylphosphine [derived from $Pd(PPh_3)_4$]. Owing to difficulties encountered with TPPO removal, the yields were determined from ^1H NMR spectra by the integration of the CH_2O signals of germatranes and 1,2-diphenoxyethane used as a standard (86, 42, and 81% for **3a**, **3b**, and **3c**, respectively). In contrast to the rhodium-catalyzed reaction, the palladium-catalyzed addition to **3a** resulted in the (*E*)-olefin as the major product regardless of solvent used (Table 1, entries 8, 9). Using toluene as solvent under reflux conditions not only shortened the reaction time but also improved the yield in the case of the 4-methyl analogue, **3b** (75% vs 42%).

Conclusion

We have shown that the addition of germatrane, $HGe(OCH_2CH_2)_3N$, to terminal aryl acetylenes is catalyzed by $[Cp^*RhCl_2]_2$ and yields styrylgermatranes. The stereochemistry of the double bond in the product can be controlled by the choice of solvent. In methylene chloride, (*E*)-*β*-styrylgermatranes are the major products, whereas in toluene (*Z*)-*β*-styrylgermatranes are the major products. The same addition is also catalyzed by $Pd(PPh_3)_4$; however (*E*)-*β*-styrylgermatranes are produced regardless of solvent. The rhodium catalyst is more efficient, offers the ability to select the stereochemistry of the product, and avoids contamination of the product with triphenylphosphine oxide.

These methods provide routes to styryl germatranes that can be used as reagents in environmentally friendly "tin-free" Stille-type cross-coupling reactions.[5]

Experimental Section

General Data. Most synthetic manipulations were carried out using standard Schlenk techniques under an inert atmosphere. Dry solvents were used unless noted otherwise. ^1H NMR spectra were recorded on either a Bruker 500 MHz or Bruker 400 MHz spectrometer, and chemical shifts are reported in ppm relative to TMS by calibration from residual protons in the deuterated solvent signals. Methylene resonances of the germatranes are reported as triplets, but these are apparent triplets arising from an AA′BB′ system. $^{13}C\{^1H\}$

(6) Ignatovich, L.; Belyakov, S.; Popelis, Yu; Lukevics, E. *Chem. Heterocycl. Compd.* **2000**, *36*, 603−606.

(7) These authors reported two doublets due to vinyl protons at *δ* 6.38 and 6.44 in $CDCl_3$. In fact, one doublet is at *δ* 6.41 while another one overlaps with phenyl signals in the range *δ* 7.19−7.28, which is clear from the integration data as well as from the $^{13}C-^1H$ correlation spectrum (HMQC). In addition, in d_4-MeOH the second vinyl signal can be observed displaced from the aromatic protons. Our $^{13}C\{^1H\}$ NMR data do not agree with those authors. The biggest discrepancy is for the vinyl carbon bound to germanium, which was reported to have a chemical shift of *δ* 88.1 in $CDCl_3$. Our results show that both olefinic carbon atoms have chemical shifts in the expected range (*δ* 120−150) at *δ* 125.3 and 144.9.

NMR spectra were recorded on either a Bruker 500 MHz or Bruker 400 MHz spectrometer operating at 125.8 and 100.6 MHz, respectively, and referenced using carbon in the solvent.

Germatrane 1. Compound **1** was prepared using a modification of the procedure of Mironov et al.[3a] A 100 mL Schlenk flask equipped with a stirring bar and rubber septum was charged with 3.00 mL of $GeCl_4$ (26.3 mmol) and 30 mL of dry hexane under nitrogen atmosphere and placed in an ice−water bath. Trichlorosilane (2.70 mL, 26.7 mmol) was added by syringe. After stirring for 30 min, 3.70 mL of dry Et_3N (26.5 mmol) was added dropwise within 2 min, and the cold bath was removed. Two phases formed, which initially were red (bottom) and colorless and cloudy (top). The red color changed to yellow within minutes. After stirring for 1 h the lower phase was separated, washed with dry hexane (3 × 10 mL), and returned to the 100 mL Schlenk flask. Dry toluene (35 mL) was added under nitrogen followed by 4.6 mL of EtOH (78.4 mmol) and 11.0 mL of dry Et_3N (78.9 mmol). After stirring for 1 h, the white precipitate that formed was filtered off and washed with 80 mL of dry toluene. The filtrate and washings were combined and added to a 250 mL round-bottomed flask containing 3.929 g of triethanolamine (25.81 mmol) in 10 mL of toluene and a stirring bar. The resulting solution was stirred at room temperature for 16 h. The yellow-orange precipitate that formed was filtered off and washed with toluene. The yellow-orange precipitate was washed on the frit with 60 mL of dichloromethane, yielding a colorless filtrate, from which **1** (3.12 g, 55% yield) was obtained after solvent removal in vacuo. Pentane was added to the toluene filtrate until the combined volume was 300 mL, and the resulting white precipitate was filtered off and washed with pentane. The white precipitate was redissolved in 40 mL of dichloromethane and passed through a 0.9 mm pad of silica gel on a 30 mL frit. The pad was washed with dichloromethane (15 mL), the filtrates were combined, and the solvent was removed in vacuo. This provided an additional 0.83 g of **1** (70% combined yield) melting at 162 °C (lit.[3a] 156−158 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.77 (s, 1H, Ge*H*), 3.80 (apparent t, 6H, J = 5.7, CH_2O), 2.86 (apparent t, 6H, J = 5.7, CH_2N). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 56.7, 51.8.

***E*-β-Styrylgermatrane (*E*-4a).** A 100 mL Schenk flask equipped with a stirring bar was charged with 0.1108 g of **1** (0.504 mmol) and 0.0152 g of **2a** (0.025 mmol). Dry dichloromethane (10 mL) was added under nitrogen. After stirring for 15 min **3a** (0.055 mL, 0.50 mmol) was added via syringe. The resulting solution was stirred at room temperature for 19 h and passed through a pad of silica gel (Natland International, 200−400 mesh) on a 15 mL frit (0.7 mm). After washing with 30 mL of dichloromethane the filtrate and washings were combined, and the volatiles were removed under reduced pressure. The residue was crystallized by addition of ether followed by evaporation (0.0368 g, 23%). ^{1}H NMR (CD_3OD, 400 MHz): δ 7.42−7.20 (m, 5H, C_6H_5), 7.12 (d, 1H, J = 18.7, C*H* =), 6.32 (d, 1H, J = 18.7, C*H*═), 3.78 (t, 6H, J = 5.7, CH_2O), 2.94 (t, 6H, J = 5.7, CH_2N). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 144.9, 138.2, 128.5, 128.0, 126.9, 125.3, 56.9, 51.9. Anal. Calcd for $C_{14}H_{19}O_3NGe$: C, 52.24; H, 5.95; N, 4.35. Found: C, 52.12; H, 5.85; N, 4.14. This compound was previously prepared by a different route.[6,7]

***Z*-β-Styrylgermatrane (*Z*-4a, contains 21% of *E*-4a).** A 25 mL three-necked round-bottomed flask equipped with a stirring bar, reflux condenser, and a rubber septum was charged with 0.2199 g of **1** (1.000 mmol) and 0.0283 g of **2a** (0.046 mmol). Toluene (10 mL) was added under nitrogen followed by 0.17 mL of **3a** (1.55 mmol). The resulting solution was heated under reflux for 12 h and passed through a pad of Celite. After washing with dichloromethane and removal of solvents the residue was dissolved in 5 mL of acetonitrile and chromatographed on reversed-phase silica gel (C_8) using acetonitrile as an eluent. The title compound was obtained as a tan solid (0.2584 g, 80%). Alternatively the residue left after evaporation of toluene was dissolved in dichloromethane and passed through a pad of silica gel on a 15 mL frit (0.7 mm). After washing with dichloromethane the filtrate and washings were combined, and the volatiles were removed under reduced pressure. The residue was crystallized from diethyl ether followed by slow evaporation to yield pale yellow crystals. Colorless crystals of ***Z*-4a** suitable for X-ray analysis were grown by slow evaporation of $CHCl_3$ from a chloroform−decalin solution. ^{1}H NMR (CD_3OD, 400 MHz): δ 7.62 (d, 2H, J = 7.1, C_6H_5), 7.33−7.21 (m, 4H, C_6H_5 and C*H*═), 5.83 (d, 1H, J = 14.2, C*H*═), 3.76 (t, 6H, J = 5.6, CH_2O), 2.84 (t, 6H, J = 5.6, CH_2N). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 145.8, 139.2, 128.6, 127.8, 127.71, 127.68, 57.0, 52.4.

***E*-β-(4-Methyl)styrylgermatrane (*E*-4b).** A 100 mL Schlenk flask equipped with a stirring bar and a rubber septum was charged with 0.2203 g of **1** (1.002 mmol) and 0.0314 g of **2a** (0.051 mmol). Dichloromethane (10 mL) was added under nitrogen followed by 0.20 mL of **3b** (1.53 mmol). The resulting solution was stirred at room temperature for 84 h. The reaction mixture was filtered through a pad of Celite and washed with dichloromethane followed by solvent removal in vacuo. The crude product was dissolved in acetonitrile and chromatographed on reversed-phase silica gel (C_8) using acetonitrile as the eluent. The title compound was obtained as a colorless solid (0.100 g, 30%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32 (d, 2H, J = 7.9, C_6H_4), 7.17 (d, 1H, J = 18.6, C*H*═), 7.07 (d, 2H, J = 7.9, C_6H_4), 6.34 (d, 1H, J = 18.6, C*H*═), 3.83 (t, 6H, J = 5.6, CH_2O), 2.86 (t, 6H, J = 5.6, CH_2N), 2.30 (s, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 144.8, 137.8, 135.5, 129.1, 126.8, 123.9, 56.9, 51.8, 21.4. Anal. Calcd for $C_{15}H_{21}O_3NGe$: C, 53.63; H, 6.30; N, 4.17. Found: C, 53.82; H, 6.42; N, 4.30.

***Z*-β-(4-Methyl)styrylgermatrane (*Z*-4b) (contains 12% of *E*-isomer).** A 25 mL three-necked round-bottomed flask equipped with a stirring bar, reflux condenser, and a rubber septum was charged with 0.2195 g of **1** (1.00 mmol) and 0.0291 g of **2a**. Dry toluene (10 mL) was added under nitrogen followed by 0.20 mL of 97% **3b** (1.53 mmol). The resulting solution was heated under reflux for 12 h and filtered through a pad of Celite. After washing with dichloromethane and solvent removal the residue was dissolved in 2 mL of acetonitrile and chromatographed on reversed-phase silica gel (C_8) using acetonitrile as an eluent. The title compound was obtained as a pale orange solid (0.2300 g, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, 2H, J = 7.8, C_6H_4), 7.26 (d, 1H, J = 14.2, C*H*═), 7.09 (d, 2H, J = 7.8, C_6H_4), 5.76 (d, 1H, J = 14.2, C*H*═), 3.76 (t, 6H, J = 5.6, CH_2O), 2.83 (t, 6H, J = 5.6, CH_2N), 2.32 (s, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 145.7, 137.4, 136.2, 128.56, 128.55, 126.4, 57.0, 52.4, 21.5. Anal. Calcd for $C_{15}H_{21}O_3NGe$: C, 53.63; H, 6.30; N, 4.17. Found: C, 53.06; H, 6.30; N, 4.13.

***E*-β-(4-Chloro)styrylgermatrane (*E*-4c).** A 100 mL Schlenk flask equipped with a stirring bar and a rubber septum was charged with 0.2208 g of **1** (1.005 mmol), 0.0284 g of **2a** (0.046 mmol), and 0.2048 g of **3c** (1.500 mmol). Dichloromethane (10 mL) was added under nitrogen, and the resulting solution was stirred at room temperature for 70 h. The reaction mixture was filtered through a pad of Celite followed by washing with dichloromethane (90 mL) and solvent removal in vacuo. Acetonitrile (4−5 mL) was added to the residue, and the resulting solution was chromatographed on reversed-phase silica gel (C_8) using acetonitrile as the eluent. The product after chromatography was dissolved in 2−3 mL of dichloromethane and precipitated by addition of 50 mL of petroleum ether (bp 35−60 °C). Compound ***E*-4c** was obtained as a pale yellow solid (0.1925 g, 54%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35 (d, 2H, J = 8.5, C_6H_4), 7.23 (d, 2H, J = 8.5, C_6H_4), 7.16 (d, 1H, J = 18.6, C*H*═), 6.39 (d, 1H, J = 18.6, C*H*═), 3.85 (t, 6H, J = 5.7, CH_2O), 2.89 (t, 6H, J = 5.7, CH_2N). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 143.5, 136.8, 133.7, 128.7, 128.1, 126.4, 56.9, 51.9.

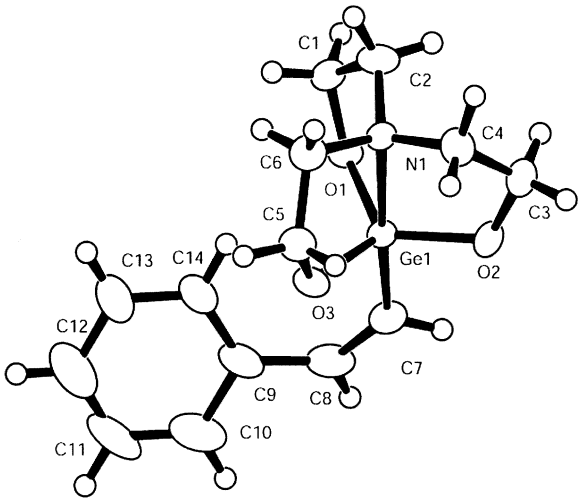


Figure 1. ORTEP diagram of (*Z*)-*β*-styrylgermatrane (*Z*-**4a**). Metrical data of interest: Ge1−C7 = 1.950(3) Å; Ge1−N1 = 2.193(2) Å; C7−C8 = 1.336(4) Å; Ge1−C7−C8 = 132.0(3)°; C7−C8−C9 = 129.6(3)°.

Anal. Calcd for $C_{14}H_{18}O_3NClGe$: C, 47.19; H, 5.09; N, 3.93. Found: C, 46.37; H, 5.06; N, 3.87.

***Z*-*β*-(4-Chloro)styrylgermatrane (*Z*-4c) (contains 15% of *E*-isomer).** A 25 mL three-necked round-bottomed flask equipped with a stirbar, reflux condenser, and a rubber septum was charged with 0.2205 g of **1** (1.003 mmol), 0.0291 g of **2a**, and 0.1659 g of **3c** (1.215 mmol). Dry toluene (10 mL) was added under nitrogen. The resulting solution was heated under reflux for 12 h and passed through a pad of Celite.[8] After washing with dichloromethane and removal of solvents the residue was dissolved in 2 mL of acetonitrile and chromatographed on reversed-phase silica gel (C_8) using acetonitrile as an eluent. The title compound, *Z*-**4c**, was obtained as a pale-orange powder (0.2410 g, 67%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.56 (d, 2H, J = 8.3, C_6H_4), 7.25−7.22 (m, 3H, C_6H_4 and C*H*═), 5.86 (d, 1H, J = 14.2, C*H*═), 3.75 (t, 6H, J = 5.6, CH_2O), 2.84 (t, 6H, J = 5.6, CH_2N). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 144.3, 137.8, 133.4, 130.0, 129.0, 127.9, 57.0, 52.4. Anal. Calcd for $C_{14}H_{18}O_3NClGe$: C, 47.19; H, 5.09; N, 3.93; Found: C, 46.96; H, 5.17; N, 3.97.

Hydrogermylation of Arylacetylenes in the Presence of Pd(PPh$_3$)$_4$ (2b). A 100 mL Schlenk flask equipped with a stirring bar was charged with 0.5 mmol of **1** and 0.025 mmol of **2b** (5 mol %) under nitrogen. THF (5 mL) was added by syringe via a septum followed by 0.6−0.8 mmol of arylacetylene **3** (1.2−1.6 equiv), and the resulting solution was stirred at room temperature for 2−4 days. The ^{1}H and ^{31}P NMR spectra of a crude product obtained after removal of solvent indicated the presence of the corresponding styrylgermatrane and TPPO. The spectra of styrylgermatranes were identical to those obtained in rhodium-catalyzed reactions. The following procedure was used for the synthesis of *E*-**4a** in toluene under reflux. A 100 mL Schlenk flask equipped with a stirring bar was charged with 0.2200 g of **1** (1.00 mmol) and 0.058 g of **2b** (0.050 mmol, 5 mol %). Toluene (10 mL) was added by syringe via a septum followed by 0.22 mL of **3a** (2.0 mmol), and the resulting solution was brought to reflux. After 17.5 h the reaction mixture was passed through a pad of Celite. Addition of ether to a residue obtained after the solvent removal resulted in precipitation of *E*-**4a** as a tan solid (0.2288 g, 71%) free of TPPO by ^{1}H NMR.

Table 2. Crystallographic Data for *Z*-4a

color, shape	colorless plate
empirical formula	$C_{14}H_{19}GeNO_3$
fw	321.90
radiation /Å	Mo Kα (monochr.) 0.71073
T/K	183
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell dimens	
a/Å	9.7012(3)
b/Å	11.2953(4)
c/Å	13.3512(6)
β/deg	107.081(2)
V/Å^3	1398.47(9)
Z	4
D_{calc}/g cm^{-3}	1.529
μ/cm^{-1} (Mo Kα)	21.93
cryst size/mm	0.048 × 0.169 × 0.169
reflns tot., unique, used[a]	11096, 3346; 2053
R_{int}	0.053
transmn range	0.661−0.911
params, restraints	172, 0
R_1,[a] wR_2,[b] *S*	0.030, 0.033, 0.94
resid density/e Å^{-3}	−0.39 < 0.34

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, for all $I > 3\sigma(I)$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Structure Determination and Refinement of *(Z)*-*β*-styrylgermatrane (*Z*-4a). Crystals were grown by slow evaporation of $CHCl_3$ from a chloroform−decalin solution. Data were collected on a Nonius KappaCCD (Mo Kα radiation) diffractometer and corrected for absorption (SORTAV[9]). The structure was solved by direct methods (SIR92[10]) and refined on *F* for all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. Relevant crystal and data parameters are presented in Table 2, and an ORTEP diagram is shown in Figure 1.

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Supporting Information Available: Detailed crystallographic data, atomic positional parameters, and bond lengths and angles for *Z*-**4a** are available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) At room temperature the reaction in toluene is very slow and gives only a trace of the addition product after 21 h. Interestingly, ^{1}H NMR indicated that this trace amount was (*E*)-**4a**, not (*Z*)-**4a**, which is the main product obtained after reflux. We have discussed the possible mechanistic implications of solvent dependence previously.[4] The relative ease of obtaining syn and anti addition products may be determined by the ease of formation and stability of an η^2-vinyl group or the formation of organometallic dimers in different solvents. These paths would provide a route for the initially formed (*Z*)-isomer to convert to the (*E*)-isomer.

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