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Stereodivergent Syntheses of (*Z*)- and (*E*)-Alkenylsilanes via Hydrosilylation of Terminal Alkynes Catalyzed by Rhodium(I) Iodide Complexes and Application to Silicon-Containing Polymer Syntheses

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$RhI(PPh_3)_3$ or $[RhI(cod)]_2$ (cod = 1,5-cyclooctadiene) as a catalyst delivers both (*Z*)- and (*E*)-alkenylsilanes in the stereodivergent hydrosilylation of terminal alkynes with heteroatom-substituted organosilane reagents. Treatment of the rhodium catalyst and the silane reagent followed by addition of terminal alkyne at room temperature leads to (*Z*)-silanes, while addition of the silane and the alkyne to the rhodium catalyst in one portion and heating at 60 °C affords (*E*)-silanes highly selectively. The obtained (*E*)- and (*Z*)-alkenylsilanes bearing heteroatom substituents on the silicon atom are subjected to the palladium-catalyzed cross-coupling reaction with aryl halides to form a carbon−carbon bond with retention of stereochemistry. The stereodivergent hydrosilylations are applied to the polyaddition with bifunctional alkynes (1,3- and 1,4-diethynylbenzene) and silanes (1,3- or 1,4-bis(dimethylsilyl)benzene), giving silicon-containing polymers, poly(aryleneethenylenesilylene)s, in highly stereocontrolled manners. A fluorine-containing silicon reagent bearing a 3,3,3-trifluoropropyl group is also subjected to the polymerization, in which $[RhI(cod)]_2$ is found to be an efficient catalyst. Measurement of UV−vis absorption/emission spectra and several thermal analyses of the polymers are also conducted.

Introduction

Hydrosilylation of an unsaturated bond with a transition metal catalyst has attracted considerable attention in organic synthesis as well as organometallic chemistry.[1] In particular, hydrosilylation to alkynes is of great interest since the reaction involves regio- and stereochemical effects to form, in the case of hydrosilylation to a terminal alkyne **1** with a silane reagent **2**, alkenylsilanes of three possible regio- and stereoisomers, *trans*-*β*- (**3**), *cis*-*β*- (**4**), and α-adduct (**5**), as shown in eq 1.

Platinum catalysts that have been frequently employed for the hydrosilylation form (*E*)-alkenylsilanes with high regio- and stereoselectivities through *cis*-*β*-addition when a chlorosilane is employed.[2] By contrast, use of alkylsilanes or alkoxysilanes results in a mixture of regioisomers.[3] On the other hand, rhodium catalysts have also been studied for the controlled hydrosilylation of alkynes. A neutral rhodium complex such as Wilkinson's catalyst, $RhCl(PPh_3)_3$ (**6**), gives (*Z*)-alkenylsilanes (**3**) with moderate to high selectivities,[4] while a cationic rhodium complex was shown to afford (*E*)-alkenylsilanes (**4**).[5] However, previous studies on the rhodium-catalyzed hydrosilylation have been mainly performed with triethylsilane, which does not possess a heteroatom substituent on silicon. Thereby, further transformation reactions of the formed alkenylsilane are considerably limited.[6] Hence, regio- and stereocontrolled synthesis

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(1) (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; pp 1479−1526. (b) Hiyama T.; Kusumoto T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 8 pp 763−792.

(2) (a) Chandra, G.; Lo, P. Y.; Hitchcock, P. B. Lappert, M. F. *Organometallics* **1987**, *6*, 191−192. (b) Iovel, I. G.; Goldberg, Y. S.; Shymanska, M.; Lukevics, E. *Organometallics* **1987**, *6*, 1410−1413. (c) Matsuhashi, H.; Asai, S.; Hirabayashi, K.; Hatanaka, Y.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1943−1952.

(3) The use of silanes with alkoxy or alkyl substituents resulted in the mixture of α- and *β*-*E*-adducts (ca. 30:70): (a) Sato, H.; Mizuno, K.; Mori, A.; Hiyama, T. Unpublished results: 70th Annual Meeting of Chemical Society of Japan, Tokyo, 1996 (3PB096). (b) Shintani, K., Ooi, O.; Mori, A.; Kawakami, Y. *Polym. Bull.* (*Berlin*) **1996**, *37*, 705−710.

(4) (a) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127−3133. (b) Faller, J. W.; Alliessi, D. G. *Organometallics* **2002**, *21*, 1743−1746, and references therein. Hydrosilylation of alkynes with other metal catalysts: (c) Doyle, M. P.; High, K. G.; Nesloney, C. L.; Clayton, T. W., Jr.; Lin, J. *Organometallics* **1990**, *10*, 1225−1226. (d) Esteruelas, M. A.; Herrero, J.; Oro, L. A. *Organometallics* **1993**, *12*, 2377−2379. (e) Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7984−7989. (e) Na, Y.; Chang, S. *Org. Lett.* **2000**, *2*, 1887−1889. (f) Kawanami, Y.; Sonoda, Y.; Mori, T.; Yamamoto, K. *Org. Lett.* **2002**, *4*, 2825−2827. (g) Chung, L. W.; Wu, Y.-D.; Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2003**, *125*, 11578−11582. (h) Katayama, H.; Taniguchi, K.; Kobayashi, M.; Sagawa, T.; Minami, T.; Ozawa, F. *J. Organomet. Chem.* **2002**, *645*, 192−200. (i) Crabtree, R. H. *New J. Chem.* **2003**, 771−772.

(5) Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Org. Chem.* **1995**, *60*, 3045−3051.

(6) Tamao, K.; Yoshida, J.; Takahashi, M.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Kurita, A.; Kumada, M. *J. Am. Chem. Soc.* **1978**, *100*, 290−292.

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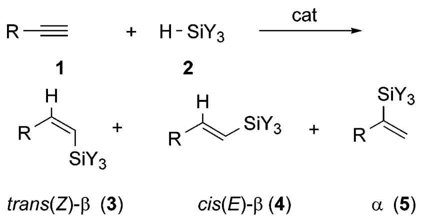
of alkenylsilanes with a silane reagent bearing heteroatom substituents is indeed of considerable interest from the viewpoint of synthetic application.

During the course of our studies on the use of siloxanes and silanols for metal-catalyzed carbon−carbon bond-forming reactions[7] we have been interested in the stereocontrolled hydrosilylation with a silicon reagent bearing heteroatom substituents and we learned that selectivities of the hydrosilylation with such silane reagents catalyzed by rhodium or platinum are much different from those of alkylsilanes and halosilanes. Herein, we report that an iodorhodium complex exhibits remarkable reactivity and selectivity in the hydrosilylation of terminal alkynes with heteroatom-containing silane reagents. *Using the same catalyst with slight modification of the reaction protocol, both (E)- and (Z)-alkenylsilanes are obtained highly selectively*. Since the produced (*E*)- and (*Z*)-alkenylsilanes possess heteroatom substituents on the silicon atom, the alkenylsilanes can be subjected to stereospecific carbon−carbon bond-forming cross-coupling reactions with a palladium catalyst.

In addition, we describe application of the stereodivergent hydrosilylation for the preparation of silicon-containing polymers, poly(aryleneethenylenesilylene)s. Since poly(aryleneethenylene)s have been shown to exhibit remarkable characteristics as conductive polymers[8] and electroluminescent (EL) materials,[9] incorporation of a silylene moiety to such polymers[10] attracts much attention in relation to conductive and light-emitting characteristics by the incorporation of the silicon atom. Although the stereochemistry of the ethenylene moiety has also been of particular interest, such studies have not been performed so far due to the lack of effective synthetic methodology. Characterizations of the stereocontrolled (*E*)- and (*Z*)-poly(phenyleneethenylenesilylene)s[11] prepared by rhodium-catalyzed hydrosilylation are also discussed.[12,13]



(1)

Results and Discussion

Stereodivergent Hydrosilylation of Terminal Alkynes with Rhodium Catalyst. In relation to our studies on the introduction of an alkenyl group into siloxane,[14] we have been searching for an efficient catalyst for the hydrosilylation of a terminal alkyne with several oligosiloxanes bearing an Si−H moiety. Although Wilkinson's complex, $RhCl(PPh_3)_3$ (**6**),[15] showed little efficiency in the regio- and stereoselectivities as well as the reactivity, addition of sodium iodide to the reaction mixture was found to enhance the reactivity. Thus, we studied the hydrosilylation of terminal alkynes with a simpler silane reagent bearing a silicon−oxygen bond such as disiloxane. When the reaction was applied to the hydrosilylation of phenylethyne (**1a**) with pentamethyldisiloxane ($HMe_2SiOSiMe_3$, **2a**) in the presence of **6** (0.1 mol %) and NaI (5 mol %), (*Z*)-(2-phenylethenyl)pentamethyldisiloxane (**3aa**) was furnished exclusively. The reaction with $RhI(PPh_3)_3$ (**7**),[16] which, we consider, is the resultant of the reaction of **6** and NaI, also underwent hydrosilylation to give **3aa** highly selectively. As represented in eq 2, treatment of **7** (0.1 mol %) and $HMe_2SiOSiMe_3$ (**2a**) at 0 °C for 2 h followed by addition of **1a** gave (*Z*)-(2-phenylethenyl)pentamethyldisiloxane (**3aa**) highly selectively after stirring at room temperature for 2 h.

Table 1 summarizes the results of the hydrosilylation of various silanes and terminal alkynes under several conditions with a rhodium catalyst. Use of Wilkinson's complex (**6**) as a catalyst under similar conditions

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(7) (a) Koike, T.; Du, X.; Sanada, T.; Danda, Y.; Mori, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 89−91. (b) Koike, T.; Mori, A. *Synlett* **2003**, 1850−1852. (c) Koike, T.; Du, X.; Mori, A.; Osakada, K. *Synlett* **2002**, 301−303. (d) Fujii, T.; Koike, T.; Mori, A.; Osakada, K. *Synlett* **2002**, 298−300. (e) Fujii, T.; Koike, T.; Mori, A.; Osakada, K. *Synlett* **2002**, 295−297. (f) Mori, A.; Danda, Y.; Fujii, T.; Hirabayashi, K.; Osakada, K. *J. Am. Chem. Soc.* **2001**, *123*, 10774−10775. (g) Mori, A.; Suguro, M. *Synlett* **2001**, 845−847. (h) Hirabayashi, K.; Mori, A.; Kawashima, J.; Suguro, M.; Nishihara, Y.; Hiyama, T. *J. Org. Chem.* **2000**, *65*, 5342−5349. (i) Hirabayashi, K.; Ando, J.; Kawashima, J.; Nishihara, Y.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1409−1417. (j) Mori, A.; Toriyama, T.; Kajiro, T.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Chem. Lett.* **1999**, 549−550.

(8) (a) Garnier, F. *Angew. Chem., Int. Ed. Engl.* **1989** *28*, 513−517. (b) Yamamoto, T. *Prog. Polym. Sci.* **1992** *17*, 1153−1205.

(9) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121−127.

(10) (a) Corriu, R. J. P.; Guerin, C.; Henner, B.; Kuhlmann, T.; Jean, A.; Garniner, F.; Yassar, J. *Chem. Mater.* **1990**, *2*, 351−352. (b) Hua, C.-H.; West, R. *Appl. Organomet. Chem.* **1994**, *8*, 423−430. (c) Ohshita, J.; Kanaya, D.; Ishikawa, M.; Koike, T.; Yamanaka, T. *Macromolecules* **1991**, *24*, 2106−2107. (d) Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1990**, *23*, 4485−4486. (e) Fang, M.-C.; Watanabe, A.; Matsuda, M. *Chem. Lett.* **1994**, 13. (f) Corriu, R. J. P.; Douglas, W. E.; Yang, Z.-X.; Garnier, F.; Yassar, A. *J. Organomet. Chem.* **1991**, *417*, C50−52. (g) van Walree, C. A.; Roest, M. R.; Schuddeboom W.; Jenneskens, L. W.; Verhoeven, J. W.; Warman, J. M.; Kooijman, H.; Spek, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 8395−8407. (h) Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 5365−5366. (i) Ishikawa, M.; Hasegawa, Y.; Kunai, A. *J. Organomet. Chem.* **1990**, *381*, C57−59. (j) Kim, H. K.; Ryu, M.-K.; Lee, S.-M. *Macromolecules* **1997**, *30*, 1236−1239. (k) Brouwer, J. H.; Krasnikov, V. V.; Hilberer, A.; Hadziioannou, G. *Adv. Mater.* **1996**, *8*, 935−937. (l) Itoh, M.; Mitsuzuka, M.; Iwata, K.; Inoue, K. *Macromolecules* **1994**, *27*, 7917−7919. (m) Majchrzak, M.; Itami, Y.; Marciniec, B.; Pawluc, P. *Tetrahedron Lett.* **2000**, *41*, 10303−10307.

(11) Polyaddition via hydrosilylation: (a) Chen, R. M.; Chien, K.-M.; Wong, K.-T.; Jin, B.-Y.; Luh, T.-Y.; Hou, J.-H.; Fann, W. *J. Am. Chem. Soc.* **1997**, *119*, 11321−11322. (b) Kunai, A.; Toyoda, E.; Nagamoto, I.; Horio, T.; Ishikawa, M. *Organometallics* **1996**, *15*, 75−83. (c) Pang, Y.; Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1993**, *26*, 5671−5675. (d) Mori, A.; Sato, H.; Mizuno, K.; Hiyama, T.; Shintani, K.; Kawakami, Y. *Chem. Lett.* **1996**, 517−518. (e) Shintani, K.; Ooi, O.; Mori, A.; Kawakami, Y. *Polym. Bull. (Berlin)* **1997**, *38*, 1−5. (f) Li, Y.; Kawakami, Y. *Macromolecules* **1998**, *31*, 5592−5597. (g) Itsuno, S.; Chao, D.; Ito, K. *J. Polym. Sci. Part A* **1993**, *31*, 287−291. (h) Tsumura, M.; Iwahara, T.; Hirose, T. *Polym. J.* **1995**, *10*, 1048−1053. (i) Dvornic, P.; Gerov, V. V.; Govedarica, M. N. *Macromolecules* **1994**, *27*, 7575−7580. (j) Kwak, G.; Masuda, T. *Macromol. Rapid Commun.* **2001**, *22*, 1233−1236. (k) Wang, F.; Kaafarani, B. R.; Neckers, D. C. *Macromolecules* **2003**, *36*, 8225−8230.

(12) Preliminary communications: (a) Mori, A.; Takahisa, E.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Chem. Lett.* **1998**, 443−444. (b) Mori, A.; Takahisa, E.; Kajiro, H.; Nishihara, Y.; Hiyama, T. *Macromolecules* **2000**, *33*, 1115−1116. See also: (c) Mori, A.; Takahisa, E.; Nishihara, Y.; Hiyama, T. *Can. J. Chem.* **2001**, **79**, 1522−1524. (d) Nishihara, Y.; Takemura, M.; Osakada, K. *Organometallics* **2002**, *21*, 825−831.

(13) A part of the results was presented in OMCOS X (International Conference on Organometallic Chemistry Directed Towards Organic Synthesis) in Versailles, 1999: Mori, A.; Takahisa, E.; Kajiro, H.; Nishihara, Y.; Hiyama, T. *Polyhedron* **2000**, *19*, 567−568.

(14) (a) Hirabayashi, K.; Mori, A.; Hiyama, T. *Tetrahedron Lett.* **1997**, *38*, 461−464. (b) Hirabayashi, K.; Takahisa, E.; Nishihara, Y.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2409−2415.

(15) Young, J. F.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1965**, 131.

(16) Hartley, F. R.; Murray, S. G.; Potter, D. M. *J. Organomet. Chem.* **1983**, *254*, 119−126.

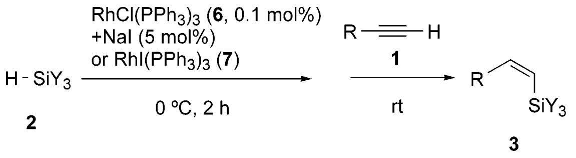
Table 1. Stereoselective Hydrosilylation of Terminal Alkynes with Hydrosilanes Bearing Heteroatom Substituents Leading to (*Z*)-Alkenylsilanes[a]

			conditions				
alkyne	$HSiY_3$	catalyst[b]	time, h	temp, °C	product	conv %[b]	ratio *E*:*Z*[c]
$C_6H_5C{\equiv}CH$ (**1a**)	$HSiMe_2OSiMe_3$ (**2a**)	A (0.1)	3	rt	**3aa**	100	1:>99
		B (0.1)	2			100	1:>99
		6 (0.1)	2			26	54:46
	$HSiMe_2OEt$ (**2b**)	B (0.1)	16		**3ab**	100	10:90
	$HSiMe(OEt)_2$ (**2c**)	B (0.1)	2		**3ac**	>95	7:93
		B (0.01)	48	60		100	2:98
	$HSi(OEt)_3$ (**2d**)	B (0.1)	16	rt	**3ad**	20	40:60
4-$MeC_6H_4C{\equiv}CH$ (**1b**)	**2a**	A (0.1)	2		**3ba**	100	0:100
	2c	B (0.1)	16		**3bc**	>95	4:96
4-$MeOC_6H_4C{\equiv}CH$ (**1c**)	**2a**		4		**3ca**	100	2:98
4-$MeCOC_6H_4C{\equiv}CH$ (**1d**)			16		**3da**	100	2:98
3-ethynylquinoline (**1e**)			48		**3ea**	40	10:90
${}^nC_6H_{13}C{\equiv}CH$ (**1f**)			48		**3fa**	>95	13:83
	2c	B (0.005)	48	80	**3fc**	100	3:97
${}^nC_4H_9C{\equiv}CH$ (**1g**)		B (0.01)	64	30	**3gc**	>95	4:96

[a] Reactions were carried out with pretreatment of a silane reagent (1 mmol) and a catalyst at 0 °C for 2 h followed by the addition of an alkyne (1 mmol). [b] A: $RhCl(PPh_3)_3$ (**6**) with NaI (5 mol %); B: $RhI(PPh_3)_3$ (**7**). [c] Estimated by ^1H NMR with 1,1,2-trichloroethylene as an internal standard. [d] Ca. 4% of α-adduct was obtained.

afforded only 26% of the product with the stereoselectivity of ca. 50:50. The reaction of alkoxysilanes, $HSiMe_2(OEt)$ (**2b**) and $HSiMe(OEt)_2$ (**2c**), with **7** afforded the (*Z*)-alkenylsilane as a major product in excellent yield and selectivity, while $HSi(OEt)_3$ (**2d**) was revealed to be ineffective. Other terminal alkynes (**1b**–**g**) with an alkyl substituent as well as an aryl group also underwent hydrosilylation to afford the corresponding (*Z*)-alkenylsilane.

Studies on the hydrosilylation of terminal alkynes have been mainly carried out with the Wilkinson's complex so far. Most of these are studied with triethylsilane as a representative silicon reagent[4,5] The reaction with a silane reagent bearing heteroatom substituents on silicon instead of triethylsilane is generally less reactive. Thus, a higher temperature that would cause inferior selectivities had to be applied when the hydrosilylation of a heteroatom-substituted silane reagent was carried out with Wilkinson's catalyst. By contrast, rhodium iodide species showed higher reactivity, which would enable the hydrosilylation with a silane reagent bearing a heteroatom at room temperature with a small amount of catalyst loading.



(2)

On the other hand, (*E*)-alkenylsilanes were obtained *with the same catalyst* by modifying the reaction conditions slightly. When the mixture of phenylethyne (**1a**), pentamethyldisiloxane (**2a**), and 0.1 mol % of **7** was treated at 60 °C for 1 h, the corresponding alkenylsilane was obtained in a quantitative yield with the regio- and stereoselectivities of **3aa**:**4aa**:**5aa** = <1:99:0 (eq 3). The results on the *E*-selective synthesis of alkenylsilanes are summarized in Table 2. The reaction of arylalkynes with several silane reagents afforded *E*-alkenylsilanes highly selectively.

Table 2. Stereoselective Hydrosilylation of Alkyne 1 Leading to (*E*)-alkenylsilanes[a]

alkyne	$HSiY_3$	time, h	product	conv, %	ratio, *E*:*Z*
1a	**2a**	1	**4aa**	100	100:0
		1		100	100:0[b]
	2c	1	**4ac**	100	100:0
	2d	1	**4ad**	100	100:0[c]
	$HSiEt_3$ (**2e**)	5[d]	**4ae**	100	100:0
1b	**2a**	1	**4ba**	100	100:0[b]

[a] The reactions were carried out using alkyne (1 mmol), $HSiY_3$ (1–1.2 mmol), and $RhI(PPh_3)_3$ (**7**, 0.1 mol %) at 55–60 °C. [b] $RhCl(PPh_3)_3$ (0.1 mol %)/NaI (5 mol %) was used as a catalyst system. [c] Two mmol of **2d** was employed. [d] The reaction was carried out at room temperature.

To obtain such a high *E*-selectivity, it appears important to perform simultaneous addition of the alkyne, the silane reagent, and the catalyst. The difference of the reaction temperatures (55–60 °C vs room temperature) is not the crucial factor of the *E*-selective hydrosilylation. Indeed, the reaction at 55 °C under the standard conditions giving *Z*-product, which involved pretreatment of **2a** with 0.1 mol % of **7**, still resulted in the (*Z*)-alkenylsilane **3aa** as a major product. Although highly *E*-selective hydrosilylation of terminal alkynes with $HSiEt_3$ (**2e**) was shown by Takeuchi with a cationic rhodium complex,[5] the reaction is applicable only to alkylalkynes. Since a cationic rhodium complex is shown to catalyze the polymerization of arylalkynes,[17] the reaction of phenylethyne afforded the hydrosilylation product in a rather lower yield.[18] By contrast, use of the iodorhodium catalyst **7** at 60 °C did not cause the polymerization of phenylethyne at all.

The mechanism for the preference of (*E*)-silanes (*cis* addition) with a cationic rhodium catalyst is explained as a rapid reductive elimination of intermediate silylrhodium species,[5] while several metal catalysts are suggested to cause isomerization through the zwitterionic or metallacyclopropene species as suggested by Ojima or Crabtree/Trost leading to the *Z*-product result-

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(17) The reactions of aryl-substituted alkynes such as phenylethyne cause undesirable polymerization to give polyalkynes: (a) Tabata, M.; Yang, W.; Yokota, K. *Polym. J.* **1990**, *22*, 1105–1107. (b) Kishimoto, Y.; Miyatake, T.; Ikariya, T.; Noyori, R. *Macromolecules* **1996**, *29*, 5054–5055. (c) Goldberg, Y.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1994**, 1209–1210.

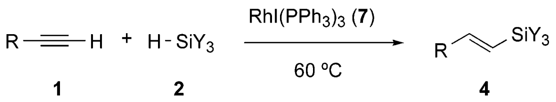
(18) The attempted hydrosilylation of phenylethyne using a catalytic amount of $[RhCl(cod)]_2$ also caused polymerization.

Table 3. Cross-Coupling of (*Z*)- and (*E*)-Alkenylsilanes[a]

alkenylsilane (*Z*/*E*)	halide	catalyst (mol %)	temp, °C	time	% yield (*Z*/*E*)
(*Z*)-PhCH=CHSiMe(OEt)$_2$ **3ac** (98/2)	I-C$_6$H$_5$ (**8a**)	[η^3-(C$_3$H$_5$)PdCl]$_2$(2.5)−PPh$_3$ (5)	60	6 h	86 (91/9)
(*Z*)-^{n}HexCH=CHSiMe(OEt)$_2$ **3fc** (97/3)	**8a**		rt	19 h	>99 (>95/5)
(*Z*)-PhCH=CHSiMe$_2$OSiMe$_3$ **3aa** (>99/1)	4-I-C$_6$H$_4$-OMe (**8b**)	Pd$_2$(dba)$_3$·CHCl$_3$ (5)	60	2 h	no reaction
(*E*)-PhCH=CHSiMe$_2$OSiMe$_3$ **4aa** (1/>99)	**8a**		rt	10 min	91 (1/>99)
4aa (1/>99)	**8b**				90 (1/>99)
4aa (1/>99)	4-I-C$_6$H$_4$-COMe (**8c**)				85 (1/>99)
4aa (1/>99)	4-I-C$_6$H$_4$-NO$_2$ (**8d**)				84 (1/>99)
4aa (1/>99)	1-naphthyl-I (**8e**)				94 (1/>99)
4aa (1/>99)	4-Br-C$_6$H$_4$-CN (**8f**)		rt	22 h	57 (1/>99)
(*Z*)-^{n}HexCH=CHSiMe$_2$OSiMe$_3$ **3fa** (94/5)	**8b**		rt	10 min	82 (94/5)
3fa (>99/1)	**8d**				76 (>99/1)
3fa (>99/1)	**8c**				93 (>99/1)
(*E*)-^{n}HexCH=CHSiMe$_2$OSiMe$_3$ **4fa** (1/>99)[b]	**8b**				95 (<1/99)[c]
4fa (1/>99)[b]	**8c**				86 (<99/1)[c]
4fa (1/>99)[b]	**8d**				81 (<99/1)[c]

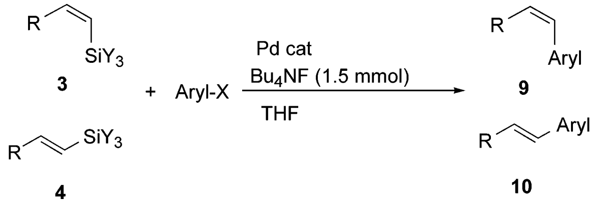
[a] The reaction was carried out with 1.2 mmol of alkenylsilane, 1.0 mmol of aryl halide, and 2.0 mmol of TBAF in 5 mL of THF. [b] The alkenylsilane contained 23% of the regioisomer **5fa**. [c] The product contained 22% of the regioisomer 2-aryl-1-octene.

ing in *trans* hyrdosilylation.[4a,g,i] Indeed, the reaction of iodorhodium catalyst leading to (*Z*)-alkenylsilane **3** would proceed in a similar manner. On the other hand, we consider that the formation of (*E*)-alkenylsilanes with an iodorhodium catalyst takes place through the isomerization of once formed (*Z*)-alkenylsilanes **3** since we have shown that **3** isomerizes to (*E*)-silane **4** in the presence of a rhodium catalyst and a catalytic amount of a silane reagent at 60 °C through addition−elimination of Rh−H species toward **3**.[12c] Although the details are not clear, pretreatment of a silane reagent with iodorhodium catalyst would form a rhodium species that is not effective for the isomerization through the addition−elimination process.[12d] Hence, the reaction involving the pretreatment procedure would not result in the formation of **4** at 60 °C.



(3)

Transformation Reactions of the C−Si Bond of Alkenylsilanes. With the stereodivergent preparation of (*Z*)- and (*E*)-alkenylsilanes in hand, transformation of the carbon−silicon bond was carried out. The carbon−carbon bond formation of alkenylsilanes with organic halides was shown to proceed in the presence of a palladium catalyst.[19,20] These reactions occur when an alkenylsilane reagent possesses at least one heteroatom substituent on the silicon atom. Hence, the cross-coupling of alkenyltriethylsilane hardly takes place. By contrast, (*E*)- and (*Z*)-alkenylsilanes bearing heteroatom substituents prepared by the catalysis of a rhodium iodide complex via stereodivergent hydrosilylation show an advantage for the palladium-catalyzed coupling reactions. As shown in Table 3, (*Z*)-alkenyl(diethoxy)methylsilane (**3ac**), bearing a phenyl substituent, and (*Z*)-1-octenyl(methyl)diethoxysilane (**3fc**) coupled with an organic halide catalyzed by a palladium complex. The reaction of iodobenzene (**8a**) was carried out with 2.5 mol % of [η^3-(C$_3$H$_5$)PdCl]$_2$ and 5 mol % of PPh$_3$ in the presence of tetrabutylammonium fluoride (TBAF).[20] The reaction of **3ac** (*Z*/*E* = 98:2) afforded the coupling product in 86% yield with the ratio of 9:91 after stirring at 65 °C for 6 h. The reaction of **3fc** (*Z*/*E* = 97:3) also yielded the product (*Z*/*E* = >95:5) at room temperature for 19 h. In addition, cross-coupling of alkenylsilanes bearing a pentamethyldisiloxy group was carried out with the Denmark's protocol.[21] Coupling of (*Z*)- and [(*E*)-1-octenyl]pentamethyldisiloxanes (**3fa** and **4fa**) proceeded in highly stereospecific manners to afford the coupling products of *Z*- and *E*-configurations (**9** and **10**), respectively. The reaction with [(*E*)-2-phenylethenyl]pentamethyldisiloxane (**4aa**) also took place, while the coupling with [(*Z*)-2-phenylethenyl]pentamethyldisiloxane (**3aa**) resulted in no reaction.



(4)

Stereodivergent Synthesis of (*E*)- and (*Z*)-Poly(phenylenesilyleneethenylene)s via Hydrosilylation Polyaddition. The rhodium-catalyzed hydrosilylations to give (*E*)- and (*Z*)-alkenylsilanes were then applied to the stereodivergent synthesis of polymers containing a silylene moiety in the main chain. With bifunctional alkyne and silane reagents we envisaged the rhodium-catalyzed polyaddition leading to (*E*)- and (*Z*)-poly(aryleneethenylenesilylene)s. The polymerization was examined using 1,*m*-diethynylbenzene (**11** and

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(19) For reviews: (a) Hatanaka Y.; Hiyama, T. *Pure Appl. Chem.* **1994**, *66*, 1471−1478. (b) Hiyama, T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998; Chapter 10, pp 421−453.

(20) (a) Tamao, K.; Kobayashi, K.; Ito, Y. *Tetrahedron Lett.* **1989**, *30*, 6051−6054. (b) Hosoi, K.; Nozaki, K.; Hiyama, T. *Chem. Lett.* **2002**, 138−139.

(21) (a) Denmark, S. E.; Wehrli, D. *Org. Lett.* **2000**, *2*, 565−568. (b) Denmark, S. E.; Wang, Z. *Org. Lett.* **2001**, *3*, 1073−1076.

Scheme 1

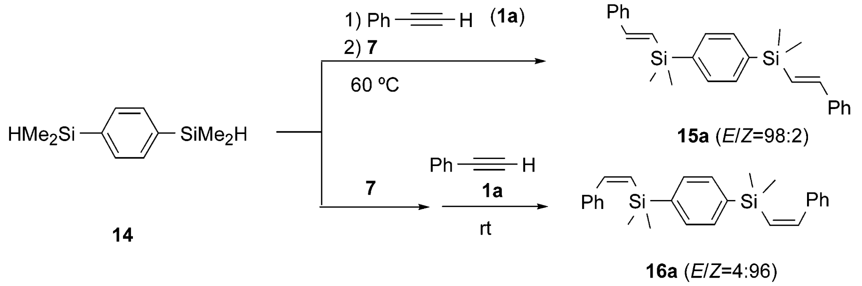
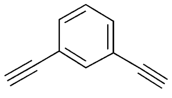


Table 4. Syntheses of 17−24 by $RhI(PPh_3)_3$-Catalyzed Hydrosilylation Polyaddition

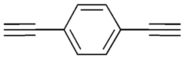
product	monomers		% yield[a]	E/Z[b]	M_n[c]	M_w/M_n[c]
	silane	alkyne				
17	**14**	**12**	88	96:4	20000	5.5
18	**13**	**12**	74	93:7	10000	5.2
19	**14**	**11**	98	96:4	12000	3.5
20	**13**	**11**	74	96:4	12000	3.9
21	**14**	**12**	70	4:96	9400	2.4
22	**13**	**12**	73	9:91	8400	2.7
23	**14**	**11**	93	3:97	8500	3.8
24	**13**	**11**	91	3:97	5900	2.6
15a	**14**	**1a**	77	98:2	399[d]	
16a	**14**	**1a**	54	4:96	399[d]	

[a] Isolated yield. [b] The ratio was determined by ^1H NMR. [c] Estimated by SEC unless noted. Detailed conditions: See Experimental Section. [d] The molecular weight calculated.

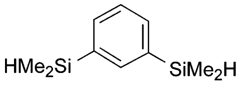
12) and 1,*n*-bis(dimethylsilyl)benzene (**13** and **14**), as monomers (*m*, *n*: 3 or 4).



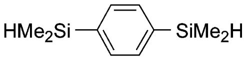
11



12



13



14

Scheme 1 shows a model study for the polyaddition with ethynylbenzene and 1,4-bis(dimethylsilyl)benzene (**14**) under the conditions to form *E*-silanes; the reaction of **1a** (2.0 mmol) and **14** (1.1 mmol) in the presence of 0.1 mol % of **7** at 80 °C for 2 h afforded the (*E*)-silane **15a** with high selectivity (>95%) in >99% yield. Characteristic signals of the ^1H NMR spectrum at δ 6.60 and 6.98 (doublet, $J = 19.2$ Hz, respectively) of **15a** suggest formation of the (*E*)-alkenylsilane. On the other hand, under the conditions to form (*Z*)-alkenylsilanes, treatment of 0.1 mol % of **7** and **14** (1.0 mmol) at 0 °C for 1 h followed by addition of **1a** (2.0 mmol) afforded bis-[(*Z*)-alkenylsilane] **16a** in a quantitative yield after stirring at room temperature for 4 h (^1H NMR δ 6.00 and 7.50, doublet, $J = 15.0$ Hz).

Bifunctional dialkynes (**11** and **12**) and silanes (**13** and **14**) were then subjected to the polymerization. As shown in Table 4, stereochemistry of the ethenylene moiety of polymers **17**−**24**, which are shown in Chart 1, was highly controlled. The obtained polymers were soluble in THF or chloroform. It should be noted that introduction of the silicon atom into the main chain of the polymer caused drastic improvement of the solubility compared with the corresponding unsubstituted poly(aryleneethenylene)s. Accordingly, the polymers with *E*-configurations, **17**−**20**, were purified by simple reprecipitation−filtration procedures, suggesting relatively good crystallinity. However, the polymer **20** derived from **11** and **13** (both meta-substituted monomers) was obtained as a gummy paste. On the other hand, only *Z*-polymer **21**, which was composed of para-substituted phenylene moieties, was obtained as a solid by reprecipitation. The other *Z*-polymers **22**−**24** appeared to be glassy at ambient temperature.

The ratios of regio- and stereoselectivities were estimated by ^1H NMR analyses, in which signals of the proton at the ethenylene moiety showed good correspondence with those of the model compounds **15a** and **16a**. As a result, the ratio of stereochemistry (*E*/*Z*) was found to be as high as 90%, while no α-adduct, which was the regioisomer in the hydrosilylation, was observed. In addition, neither isomerization of the ethenylene nor decomposition of the polymer was observed during the isolation and purification procedures. Molecular weights (M_n) of **17**−**24** obtained were found to be 6000−20000 and their molecular weight distributions were in the range 2.4−5.5 on the basis of SEC analyses. Molecular weights of the polymer of *E*-configuration appear to be generally higher than those of the corresponding Z-polymer.

The reaction with the bifunctional silicon compounds 1,3-bis[methyl(3,3,3-trifluoropropyl)silyl]benzene (**25**) and 1,4-bis[methyl(3,3,3-trifluoropropyl)silyl]benzene (**26**) bearing a 3,3,3-trifluoropropyl group on the silicon atom was also found to proceed.[22] First, the attempted hydrosilylation with $RhI(PPh_3)_3$ (**7**) was not successful probably due to the steric congestion compared with that of dimethylsilyl derivatives **13** and **14**. However, polymerization occurred by switching the rhodium catalyst to $[RhI(cod)]_2$ (**27**) to give polymers **28**−**35** shown in Chart 2. Table 5 summarizes the results. Polymers were isolated successfully except *E*-polymer **31**, composed of 1,3-dialkyne **11** and 1,3-bis-silane **25**, which would be indeed produced but failed to be isolated because of inferior crystallinity.

Spectroscopic characteristics and thermal properties of polymers **17**−**24** and **28**−**35** are summarized in Table 6. Measurement of UV−vis spectra suggested that remarkable conjugation through the silicon atom was

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[22] Although the monomers **30** and **31** were potentially a mixture of diastereomers, these were hardly separated and distinguished by NMR analyses in both monomers and polymers.

Chart 1

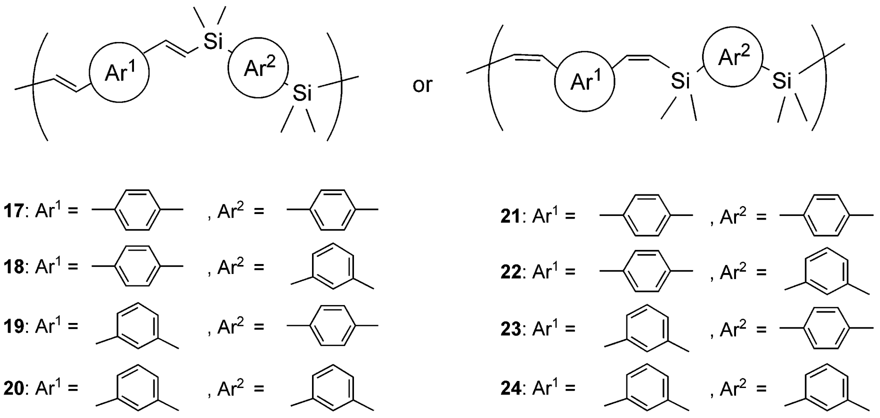

Chart 2

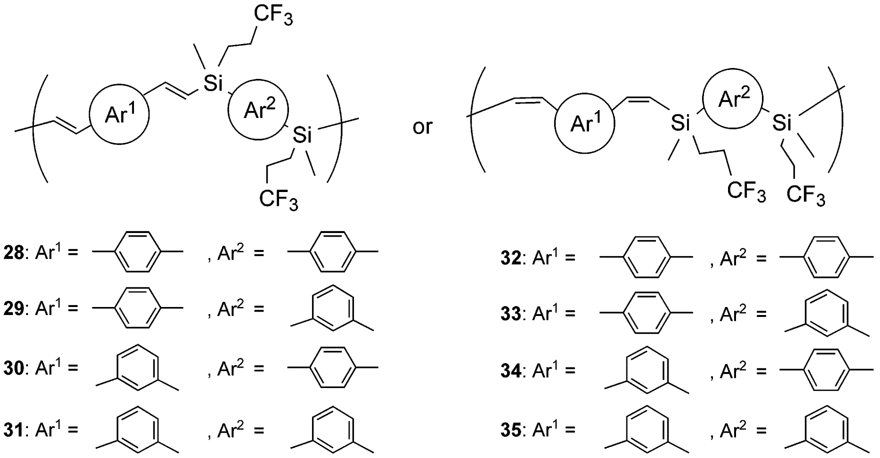

Table 5. Syntheses of 28−35 by [RhI(cod)]$_2$-Catalyzed Hydrosilylation Polyaddition

	monomers					
product	silane	alkyne	% yield[a]	E/Z [b]	M_n[c]	M_w/M_n[c]
28	**26**	**12**	96	93:7	6300	3.7
29	**25**	**12**	74	>99:1	5600	3.5
30	**26**	**11**	99	>99:1	16000	2.1
31	**25**	**11**	not obtained			
32	**26**	**12**	96	8:92	6000	5.4
33	**25**	**12**	65	6:94	9300	6.4
34	**26**	**11**	76	4:96	7300	3.2
35	**25**	**11**	61	<1:99	22000	2.8

[a] Isolated yield. [b] The ratio was determined by ^{1}H NMR. [c] Measured by SEC. Detailed conditions: See Experimental Section.

not observed.[23] These results are consistent with those of silicon-containing polymers of *E*-configuration reported by Luh.[11a] Polymers bearing the 1,4-disubstituted Ar^1 moiety showed relatively higher λ_{max} values than those of 1,3-disubstituted Ar^1, while λ_{max} values were hardly influenced by the substituted position of Ar^2 moieties.

It should be noted that all polymers were found to show light emission by the measurement of photoluminescent spectrum. Most of polymers bearing the ethenylene-*p*-phenyleneethenylene moiety, **17**, **18**, **21**, and **22**, whose λ_{max} values of absorption spectra were at ca. 300 nm, showed emission peaks at 350−360 nm. It is remarkable that polymers with ethenylene-*m*-phenyleneethenylene moieties, **19**, **20**, **23**, and **24** (λ_{max} values of UV−vis spectra were 260 or less), also exhibited Em values at 350−360 nm. These results suggest formation of an exciplex by the interaction of arylene groups between intra- or intermolecular polymer chains. Polymers **21** and **22**, which possess *p*-phenylene and *Z*-ethenylene units, also exhibited a similar shift to around 400 nm, while the related shift in the corresponding *E*-polymers was less remarkable. It should be noted that emission intensities of polymers **19** and **20** were particularly stronger.

On the other hand, polymers **28**−**35**, bearing the methyl(3,3,3-trifluoropropyl)silylene moiety, exhibited much lower intensities of light emission than those with dimethylsilylene moieties. These results suggest that fluorine-containing polymers are more flexible than the related dimethylsilylene derivative. Similar to dimethylsilylene polymers, **30**, bearing the (*E*)-ethenylene-*m*-phenylene-(*E*)-ethenylene moiety, showed the strongest light emission.

DSC analyses showed that glass transition temperatures (T_g) of *E*- and *Z*-polymers composed of 1,4-disubstituted Ar^1 and Ar^2 were found to be higher, while the values were relatively lower when each Ar^1 or Ar^2 moiety was 1,3-disubstituted. Polymers bearing both 1,3-disubstituted Ar^1 and Ar^2 groups exhibited further lower T_g values. On the other hand, *Z*-polymers showed relatively higher (5%) loss of weight values of TGA than those of the corresponding *E*-polymers, suggesting that

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(23) Conjugation through boron: Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 10776−70777.

Table 6. Spectroscopic and Thermal Properties of 17−24 and 28−35[a]

polymer	UV−vis λ_{max}, nm	ϵ, mol^{-1}	emission[b,c] Em, nm	intensity[d]	DSC T_g, °C	TGA,[e] °C weight loss 5%, 10%
17	302	27 700	352 (398)	1040 (470)	90.2	320, 392
18	302	30 100	351 (398)	876 (622)	39.2	346, 426
19	262	29 600	361 (330)	7870 (7090)	41.7	331, 396
20	260	27 600	352 (340)	6660 (5940)	28.7	386, 423
21	290	15 700	352 (398)	550 (470)	63.0	374, 444
22	288	14 500	397 (352)	705 (439)	33.0	438, 482
23	<250	24 200	352 (338)	1350 (1200)	38.1	355, 387
24	<250	25 100	353 (336)	984 (719)	*f*	273, 365
28	303	10 800	395 (354)	49 (36)	52.8	400, 433
29	285	17 900	391 (353)	31 (29)	23.4	387, 417
30	253	17 100	353 (338)	365 (332)	39.2	356, 400
32	290	33 600	398 (351)	14 (7)	55.7	423, 448
33	302	24 300	394 (353)	47 (40)	23.4	443, 466
34	261	25 100	354 (338)	363 (328)	34.5	418, 453
35	259	26 100	354 (338)	24 (20)	9.5	396, 422

[a] Analyses conditions: See Experimental Section. [b] Emission max. wavelength. The excitation wavelength is the λ_{max} values of each UV−vis spectrum. [c] In parentheses, emission wavelength and the relative intensity of the second maximum value are shown. [d] Relative intensity at Em (arbitrary units). [e] The temperature of 5% weight loss (left) and 10% weight loss (right). [f] Not detected.

Z-polymers are more thermally stable than the corresponding *E*-polymer. These results are consistent with Masuda's findings that have been recently reported on the related hydrosilylation polymerization with an AB-type monomer prepared with our protocol using RhI(PPh_3)$_3$ as a catalyst.[11j] Polymers with methyl(3,3,3-trifluoropropyl)silylene moieties exhibited relatively higher (5%) weight loss temperature values than those of the corresponding dimethylsilylene derivatives, suggesting thermally stable characteristics despite lower T_g values. These lower T_g values of fluorine-containing polymers are also consistent with the results of lower quantum yields in emission spectra.

Conclusion

In conclusion, rhodium iodide was found to serve as a regio- and stereoselective catalyst for the hydrosilylation of terminal alkynes. With the same catalyst, (*E*)- and (*Z*)-alkenylsilanes were synthesized in a stereospecific manner by slight modification of reaction conditions. Since the reaction was carried out selectively with a silane reagent bearing heteroatom substituents on the silicon atom, the obtained (*E*)- and (*Z*)-alkenylsilanes were subjected to stereospecific cross-coupling reaction with aryl halides to form a carbon−carbon bond. In addition, the stereodivergent hydrosilylation was applied for the rhodium-catalyzed polymerization with bifunctional alkynes and silanes to give silicon-containing poly(phenyleneethenylene)s. The polymerization enabled us to compare characteristics of the obtained polymers based on the stereochemistry of the ethenylene moiety. Spectroscopic and thermal analyses of obtained *E*- and *Z*-polymers revealed that characteristics of polymers are dependent on the stereochemistry of the ethenylene moiety, substituent of the silylene group, and substitution patterns of the arylene moieties.

Experimental Section

General Procedures. All temperatures were uncorrected. ^{1}H NMR (300 MHz) spectra ($CHCl_3$; 7.26 ppm as an internal standard) and ^{13}C NMR (75 MHz) spectra ($CDCl_3$; 77.0 ppm as an internal standard) were measured on a Varian Mercury 300 spectrometer, the chemical shifts being given in ppm. Yields estimated by ^{1}H NMR were based on the methyl signal of 4-methylbiphenyl as an internal standard. IR spectra were recorded with a Shimadzu FT-IR 8000A spectrometer. Mass spectra were recorded with a Shimadzu QP-5000 GC-MS system. High-resolution mass spectra were obtained on a JEOL MStation JMS 700. Elemental analyses were carried out at the Elemental Analysis Center of Chemical Resources Laboratory, Tokyo Institute of Technology, using a Yanako MTCHN Corder. UV−vis spectra were measured as a 1×10^{-5} M solution of chloroform with a JASCO V-530 spectrophotometer. Emission and excitation spectra were measured as a 3×10^{-6} M solution of chloroform with a Hitachi F-4000 fluorescence spectrometer. The photoluminescence quantum yields (Φ) were estimated with 1 M aqueous solution of quinine sulfate as a reference. SEC (size exclusion chromatography) analyses were carried out with a JASCO HPLC system equipped with a UV detector using THF as an eluent: flow rate = 1.0 mL·min^{-1} with a Shodex KF-806L column. Molecular weight and molecular weight distribution were estimated on the basis of the calibration curve obtained by standard polystyrenes. DSC analyses were carried out with a Shimadzu DSC-50. TGA was carried out with a Seiko Instruments TG/DTA-220. For thin-layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. Flash column chromatography was performed using Merck Kieselgel 60 (70−230 mesh and 230−400 mesh) or Wakogel C-200.

Penatamethyldisiloxane (**2a**), diethoxymethylsilane (**2c**), ethoxydimethylsilane (**2b**), triethoxysilane (**2d**), and chloro(methyl)(3,3,3-trifluoropropyl)silane were kindly donated by Shin-Etsu Chemical Co. Ltd. Rhodium(III) chloride trihydrate, chlorotris(triphenylphosphine)rhodium(I) (Wilkinson's catalyst), 1-octyne (**1f**), and 1-hexyne (**1g**) were purchased and used as received. Phenylethyne (**1a**), (4-methoxyphenyl)ethyne (**1c**), and (4-methylphenyl)ethyne (**1b**) were purchased and distilled under reduced pressure prior to use. Other arylalkynes were prepared from the corresponding aryl bromide or iodide with Sonogashira−Hagihara reaction, which was a coupling reaction with trimethylsilylethyne followed by base-catalyzed removal of the TMS group as shown in the literature.[24] Sodium iodide was purchased, dried at 100 °C overnight under reduced pressure (0.5 Torr), and stored under an argon atmosphere. Diethyl ether, THF, toluene, and hexane were distilled from sodium benzophenone ketyl prior to use.

Iodotris(triphenylphosphine)rhodium(I) (7).[25] To a two-necked flask equipped with a magnetic stirring bar, reflux

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[24] (a) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627−629. (b) Taylor, E. C.; Ray, P. S. *J. Org. Chem.* **1988**, *53*, 35−38.

[25] Valerino, L. *J. Chem. Soc. A* **1957**, 1711−1732.

condenser, and a rubber septum were added triphenylphosphine (2.4 g, 9.16 mmol), 80 mL of ethanol, and $RhCl_3 \cdot 3H_2O$ (0.40 g, 1.68 mmol). The reaction mixture was heated to reflux to form an orange precipitate. To this mixture was quickly added a solution of lithium iodide (1.0 g, 9.16 mmol) in 32 mL of hot ethanol, and the reaction mixture was refluxed for a further 4 h to form a brown solid, which was filtered off. Crude $RhI(PPh_3)_3$ was recrystallized from benzene to yield 50% of a dark brown crystal.

General Procedure for the Stereoselective Hydrosilylation Leading to (*Z*)-Alkenylsilanes: Procedure A. To a screw-capped glass tube were added $RhCl(PPh_3)_3$ (**6**, 1.0 mg, 0.001 mmol) and NaI (7.5 mg, 0.05 mmol), and then silane **2** (1.0 mmol) was added to the mixture, which was stirred at room temperature for 2 h. To the light-yellow-colored heterogeneous mixture was added 1-alkyne **1** (1.0 mmol) at 0 °C. When the mixture did not dissolve, a small amount of toluene (up to 3 mmol) was added to form a clear solution. Stirring was continued at room temperature, while the progress of the reaction was monitored by ^1H NMR taking an aliquot of the mixture. After the reaction was confirmed to be complete, the mixture was subjected to bulb-to-bulb distillation to yield the corresponding (Z)-alkenylsilane.

Procedure B. To a screw-capped glass tube was added $RhI(PPh_3)_3$ (**7**, 1.0 mg, 0.001 mmol), and then silane **2** (1.0 mmol) was added. The resulting mixture was stirred at room temperature for 2 h. The following procedure was performed in a manner similar to procedure A to give the corresponding (*Z*)-alkenylsilane.

Pentamethyl[(*Z*)-2-phenylethenyl]disiloxane (3aa): colorless oil; bp 110 °C (0.2 Torr, bath temp); ^1H NMR ($CDCl_3$) δ 0.04 (s, 9H), 0.10 (s, 6H), 5.75 (d, $J = 15.5$ Hz, 1H), 7.24−7.44 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 1.0, 2.2, 126.7, 128.3, 128.7, 128.8, 138.3, 144.2; IR (neat) 2959, 1607,1576, 1495, 1253, 1055, 845 cm^{-1}; HRMS calcd for $C_{13}H_{22}OSi_2$ 250.1209, found 250.1233.

Ethoxy(dimethyl)[(*Z*)-2-phenylethenyl]silane (3ab): colorless oil; bp 90 °C (0.2 Torr, bath temp); ^1H NMR ($CDCl_3$) δ 0.15 (s, 6H), 1.16 (t, $J = 7.0$ Hz, 3H), 3.64 (q, $J = 7.0$ Hz, 2H), 5.77 (d, $J = 15.1$ Hz, 1H), 7.24−7.50 (m, 6H); ^{13}C NMR ($CDCl_3$) δ −0.55, 18.33, 58.34, 127.73, 128.00, 128.27, 129.49, 139.33, 148.30; IR (neat) 3060, 3024, 2971, 2920, 2900, 2870, 1593, 1570, 1252, 1105, 1078, 947, 837, 787 cm^{-1}; HRMS calcd for $C_{12}H_{18}OSi$ 206.1127, found 206.1146.

Diethoxy(methyl)[(*Z*)-2-phenylethenyl]silane (3ac). Iodotris(triphenylphosphine)rhodium(I) (0.52 mg, 0.00052 mmol, 0.01 mol %) was added to diethoxymethylsilane (**2c**, 0.840 mL, 5.2 mmol) at 0 °C, and the mixture was stirred over a period of 2 h with gradually raising to room temperature. To the resulting pale brown solution was added phenylethyne (**1a**, 0.570 mL, 5.2 mmol) at 0 °C, and stirring was continued at room temperature for 2 h. Then the mixture was warmed to 30 °C and stirred for 64 h. The mixture was poured into 25 mL of hexanes to remove the residue of rhodium catalyst, which was filtered off through a Celite pad, and the cake was washed with 50 mL of hexanes. The combined filtrate was concentrated in vacuo to leave a crude oil, which was subjected to bulb-to-bulb distillation at 145 °C (bath temp) under reduced pressure (3 Torr) to give **3ac** as a colorless oil (80% yield): ^1H NMR ($CDCl_3$) δ 0.10 (s, 3H), 1.21 (t, $J = 6.6$ Hz, 6H), 3.76 (q, $J = 6.6$ Hz), 5.72 (d, $J = 15.3$ Hz, 1H), 7.24−7.54 (m, 6H); ^{13}C NMR ($CDCl_3$) δ −3.54, 18.24, 58.24, 125.58, 127.99, 128.06, 128.25, 138.96, 149.57; IR (neat) 3061, 2975, 2880, 1595, 1572, 1391, 1260, 1105, 1078, 953, 798 cm^{-1}; HRMS calcd for $C_{13}H_{20}O_2Si$ 236.1233, found 236.1239.

Triethoxy[(*Z*)-2-phenylethenyl]silane (3ad). The reaction was carried out in a manner similar to the synthesis of **3ac**. The product was obtained as a mixture of **3ad** and the corresponding *E*-isomer. The ratio was estimated by ^1H NMR analysis: ^1H NMR ($CDCl_3$) δ 5.68 (d, $J = 15.6$ Hz, 1H, ArCH═C*H*Si) for *Z*-isomer, 6.18 (d, $J = 19.5$ Hz, 1H, ArCH═C*H*Si) for *E*-isomer.

[(*Z*)-2-(4-Methylphenyl)ethenyl](pentamethyl)disiloxane (3ba): yield 92%; colorless oil; bp 125 °C (0.2 Torr, bath temp); ^1H NMR ($CDCl_3$) δ 0.08 (s, 9H), 0.14 (s, 6H), 2.36 (s, 3H) 5.72 (d, $J = 15.6$ Hz, 1H), 7.10−7.40 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 1.97, 2.01, 21.3, 128.4 128.7, 130.7, 136.8, 137.5, 147.0; IR (neat) 3023, 2959, 1597, 1565, 1510, 1447, 1410, 1254, 1051, 841, 810, 793, 754, 695 cm^{-1}; HRMS calcd for $C_{14}H_{24}OSi_2$ 264.1364, found 264.1357.

(Diethoxy)(methyl)[(*Z*)-2-(4-methylphenyl)ethenyl]silane (3bc): ^1H NMR ($CDCl_3$) δ 0.12 (s, 3H), 1.21 (t, $J = 6.9$ Hz, 6H), 2.35 (s, 3H), 3.78 (q, $J = 6.9$ Hz, 4H), 5.64 (d, $J = 15.6$ Hz, 1H), 7.14 (d, $J = 8.2$ Hz, 2H), 7.36 (d, $J = 15.6$ Hz, 1H), 7.41 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −3.56, 18.24, 21.52, 58.21, 124.23, 128.23, 128.77, 136.11, 137.91, 149.54; IR (neat) 2975, 2924, 2878, 1601, 1565, 1512, 1443, 1391, 1258, 1165, 1105, 1078, 951, 851, 831, 801 cm^{-1}; HRMS calcd for $C_{14}H_{22}O_2Si$ 250.1389, found 250.1390.

[(*Z*)-2-(4-Methoxylphenyl)ethenyl](pentamethyl)disiloxane (3ca): yield >99%; colorless oil; bp 130 °C (0.2 Torr, bath temp); ^1H NMR ($CDCl_3$) δ 0.07 (s, 9H), 0.14 (s, 9H), 3.82 (s, 3H), 5.65 (d, $J = 15.5$ Hz, 1H), 6.85 (d, $J = 9.1$ Hz, 2H), 7.24 (d, $J = 15.5$ Hz, 1H), 7.40 (d, $J = 9.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 1.89, 1.93, 55.25, 113.28, 129.30, 129.76, 132.25, 146.41, 159.20; IR (neat) 2957, 2903, 2838, 1609, 1510, 1254, 1040, 841 cm^{-1}; HRMS calcd for $C_{14}H_{24}O_2Si_2$ 280.1315, found 280.1314.

(*Z*)-2-(4-Acetylphenyl)ethenyl(pentamethyl)disiloxane (3da). The product was purified by column chromatography on silica gel (hexanes/Et_2O, 10:1): yield 75%; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9H), 0.12 (s, 6H), 2.61 (s, 3H), 5.92 (d, $J = 15.5$ Hz, 1H), 7.31 (d, $J = 15.5$ Hz, 1H), 7.51 (d, $J = 6.5$ Hz, 2H), 7.91 (d, $J = 6.5$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 1.84, 1.88, 26.62, 128.01, 128.50, 134.70, 135.97, 144.22, 145.54, 197.68; IR (neat) 2959, 2901, 1686, 1603, 1266, 1256, 1051, 843 cm^{-1}; HRMS calcd for $C_{15}H_{24}O_2Si_2$ 292.1315, found 292.1314.

3-[(*Z*)-2-(Dimethyl)(trimethylsiloxy)silylethenyl]quinoline (3ea). This compound was obtained as a mixture of **3ea**, the *E*-isomer **4ea**, and 3-ethynylquionline (**1i**). The ratio was estimated by ^1H NMR analysis: ^1H NMR ($CDCl_3$) δ 6.05 (d, $J = 15.5$ Hz, 1H, ArCH═C*H*Si), 7.42 (d, $J = 15.5$ Hz, 1H, ArC*H*═CHSi) for 4i; 6.67 (d, $J = 19.0$ Hz, 1H, ArCH═C*H*Si), 7.08 (d, $J = 19.0$ Hz, 1H, ArC*H*═CHSi) for the *E*-isomer; and 3.28 (s, 1H, C≡C*H*), 4.72 (m, 1H, Si*H*) for **1e**.

[(Z)-1-Octenyl](pentamethyl)disiloxane (3fa): colorless liquid; bp 85 °C (3 Torr, bath temp); ^1H NMR ($CDCl_3$) δ 0.07 (s, 9H), 0.16 (s, 6H), 0.81 (brt, $J = 7.0$ Hz, 3H), 1.21−1.42 (m, 8H), 2.05−2.21 (m, 2H), 5.41 (d, $J = 14.1$ Hz, 1H), 6.29 (dt, $J = 14.1, 7.8$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.96, 2.44, 14.10, 22.63, 29.07, 29.67, 31.81, 33.47, 128.55, 149.72; IR (neat) 2959, 2928, 2856, 1608, 1254, 1055, 843, 808, 785 cm^{-1}; HRMS calcd for $C_{13}H_{30}OSi_2$ 258.1835, found 258.1807.

Diethoxy(methyl)[(Z)-1-octenyl]silane (3fc). Iodorhodium(I) tris(triphenylphosphine) (**8**, 0.53 mg, 0.01 mol %) and diethoxymethylsilane (**2c**, 0.856 mL, 5.3 mmol) were stirred for 2 h at room temperature. To the solution was added 1-octyne (**1f**, 0.782 mL, 5.3 mmol) in one portion, and the reaction mixture was stirred for 2 days at 80 °C. The mixture was added to 5 mL of hexanes to form a precipitate, which was filtered through Florisil. The filtrate was concentrated under reduced pressure to yield a crude oil, which was subjected to bulb-to-bulb distillation to afford **3fc** as a colorless liquid (72%): bp 110 °C (3 Torr, bath temp); ^1H NMR ($CDCl_3$) δ 0.21 (s, 3H), 0.88 (t, $J = 7.2$ Hz, 3H), 1.21−1.42 (m, 14H), 2.22 (dt, $J = 6.9$ Hz, 7.5 Hz, 2H), 3.77 (q, $J = 6.9$ Hz, 4H), 5.35 (d, $J = 14.1$ Hz, 1H), 6.44 (dt, $J = 14.1, 6.9$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −2.51, 14.07, 18.33, 22.60, 29.04, 29.49, 31.75, 33.76, 58.19, 122.66, 153.17; IR (neat) 2973, 2926, 2859, 1609, 1391, 1258, 1167, 1105, 1080, 953, 799, 772 cm^{-1}; HRMS calcd for $C_{13}H_{28}O_2Si$ 244.1859, found 244.1856.

Diethoxy[(*Z*)-2-hexenyl](methyl)silane (3gc): colorless liquid; bp 90 °C (3 Torr, bath temp); ^1H NMR ($CDCl_3$) δ 0.20

(s, 3H), 0.90 (t, $J = 6.9$ Hz, 3H), 1.21 (t, $J = 6.9$ Hz, 6H), 1.32−1.39 (m, 4H), 2.17−2.28 (m, 2H), 3.75 (q, $J = 6.9$ Hz, 4H), 5.36 (d, $J = 14.1$ Hz, 1H), 6.43 (dt, $J = 14.1$, 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −2.54, 13.98, 18.31, 22.40, 31.69, 33.44, 58.06, 122.71, 153.07; IR (neat) 2973, 2926, 2876, 1609, 1391, 1258, 1167, 1105, 1080, 953, 823, 799, 772 cm^{-1}; HRMS calcd for $C_{18}H_{28}O_2Si$ 216.1546, found 216.1546.

General Procedure for the Hydrosilylation Leading to (*E*)-alkenylsilanes. To a screw-capped glass tube were added $RhCl(PPh_3)_3$ (1.0 mg, 0.001 mmol)/NaI (7.5 mg, 0.05 mmol) or $RhI(PPh_3)_3$ (**7**, 1.0 mg, 0.001 mmol), 1-alkyne **1** (1.0 mmol), and silane **2** (1.05−1.1 mmol) at room temperature. The resulting mixture was then heated at 55−60 °C until completion of the reaction was confirmed by ^{1}H NMR. Purification was carried out similarly to that of (*Z*)-alkenylsilanes by bulb-to-bulb distillation.

Pentamethyl[(*E*)-2-phenylethenyl]disiloxane (4aa): colorless oil; bp 115 °C (0.2 Torr, bath temp); ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 9H), 0.23 (s, 6H), 6.43 (d, $J = 19.2$ Hz, 1H), 6.95 (d, $J = 19.2$ Hz, 1H), 7.26−7.49 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 1.0, 2.2, 126.7, 128.3, 128.7, 128.8, 138.3, 144.2; IR (neat) 2959, 1593, 1572, 1493, 1253, 1051, 843 cm^{-1}; HRMS calcd for $C_{13}H_{22}OSi_2$ 250.1209, found 250.1223.

Diethoxy(methyl)[(*E*)-2-phenylethenyl]silane (4ac):[26] ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 3H), 1.26 (t, $J = 6.9$ Hz, 6H), 3.83 (q, $J = 6.9$ Hz, 4H), 6.31 (d, $J = 19.2$ Hz, 1H), 7.11 (d, $J = 19.2$ Hz, 1H), 7.25−7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −4.19, 18.38, 58.36, 122.40, 126.65, 128.49, 128.51, 137.72, 147.34; IR (neat) 2975, 2880, 1607, 1574, 1495, 1449, 1390, 1258, 1105, 1078, 953, 847, 820 cm^{-1}; HRMS calcd for $C_{13}H_{22}OSi_2$ 236.1232, found 236.1226.

(*E*)-2-(4-Methylphenyl)ethenyl(pentamethyl)disiloxane (4ba). The product contains a trace amount of inseparable unidentified byproduct: ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9H), 0.21 (s, 6H), 2.38 (s, 3H), 6.35 (d, $J = 19.2$ Hz, 1H), 6.89 (d, $J = 19.2$ Hz, 1H), 7.14 (d, $J = 8.0$ Hz, 1H), 7.35 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.82, 2.04, 21.24, 126.42, 127.39, 129.19, 135.52, 138.00, 143.97; IR (neat) 2959, 2901, 1608, 1510, 1410, 1256, 843, 797 cm^{-1}; HRMS calcd for $C_{14}H_{24}OSi_2$ 264.1366, found 264.1375.

(*Z*)-Stilbene (palladium-catalyzed cross-coupling of 3ac). To a solution of PPh_3 (5.42 mg, 0.5 mol %) in 0.8 mL of dry THF was added $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (3.8 mg, 0.25 mol %) at room temperature. Then, iodobenzene (**8a**, 0.050 mL, 0.45 mmol) and tetra-*n*-butylammonium fluoride (0.45 mL of 1 M THF solution, 0.45 mmol) were added, and the mixture was stirred at 0 °C for 5 min. To the resulting mixture was added **3ac** ($E/Z = 2/98$; 0.100 mL, 0.41 mmol) to form a brown-red solution and heated at 50 °C for 1 h. The mixture was poured into 20 mL of diethyl ether and stirred under aerobic conditions for 15 min to precipitate the palladium residue. The mixture was filtered off through a Celite pad. The filtrate was concentrated under reduced pressure to leave a crude oil, which was purified by column chromatography on silica gel (hexanes/diethyl ether, 20:1). Stilbene (63 mg, 86%) was obtained with the E/Z ratio of 5:95.

(*Z*)-1-Phenyl-1-octene (palladium-catalyzed cross-coupling of 3ac). The reaction was carried out in a similar manner as above using **3ac** ($E/Z = 2{:}98$) and iodobenzene with stirring at room temperature for 1.5 h to give (*Z*)-1-phenyl-1-octene ($E/Z = 5{:}95$) in 82% yield.[20]

1,3-Bis(dimethylsilyl)benzene (13).[27] To a two-necked flask were added THF (45 mL), magnesium turnings (15.1 g, 62.5 mmol), and dimethylchlorosilane (5.8 mL, 52.5 mmol). The flask was immersed in an ice bath for 5 min with stirring. After cooling, the ice bath was removed and 1,4-dibromobenzene (3.1 mL, 25 mmol) was added dropwise via a syringe. Exothermic reaction occurred, and the reaction temperature was kept under 35 °C using the ice bath. The reaction mixture was stirred at room temperature for an additional 12 h, during which the mixture turned to a gray suspension. Then, the mixture was poured into a saturated sodium bicarbonate solution (50 mL) with stirring, and the mixture was extracted twice with hexanes (30 mL). The combined organic layers were dried over anhydrous sodium sulfate. Removal of the solvent left a crude colorless oil, which was purified by bulb-to-bulb distillation at 95 °C (bath temp; 0.6 Torr) to yield **13** as a colorless oil (60%): ^{1}H NMR ($CDCl_3$) δ 0.36 (d, $J = 3.6$ Hz, 12H), 4.44 (septet, $J = 3.6$ Hz, 2H), 7.33−7.55 (m, 4H).

1,3-Bis[methyl(3,3,3-trifluoropropyl)silyl]benzene (25). To a mixture of magnesium turnings (2.6 g, 110 mmol) and chloro(methyl)(3,3,3-trifluoropropyl)silane (82.9% purity, 21.0 g, 100 mmol) in THF (70 mL) was added dropwise via syringe 1,3-dibromobenzene (4.8 mL, 40 mmol). The resulting mixture was stirred at room temperature for 12 h to form a dark gray precipitate. Then the suspension was poured into hexanes (50 mL) and washed three times with water (50 mL × 3). The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by distillation, affording 6.1 g of **25** as a colorless oil: bp 75 °C (0.7 Torr); ^{1}H NMR ($CDCl_3$) δ 0.41 (d, $J = 3.6$ Hz, 6H), 1.04−1.41 (m, 4H), 2.00−2.13 (m, 4H), 4.41 (m, 2H), 7.40 (t, $J = 6.9$ Hz, 1H), 7.56 (d, $J = 6.9$ Hz, 2H) 7.66 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −6.0, 5.5 (d, $J = 2.3$ Hz), 29.2 (q, $J = 30$ Hz), 127.5 ($J = 277$ Hz), 127.8, 134.4, 135.6, 140.1; ^{19}F NMR ($CDCl_3$) δ −69.1 (t, $J = 10.2$ Hz); IR (neat) 2965, 2128, 1443, 1366, 1314, 1266, 1210, 1127, 1069, 1030, 912, 878, 849, 826 cm^{-1}. Anal. Calcd for $C_{14}H_{20}F_6Si_2$: C, 46.91; H, 5.62. Found: C, 46.59; H, 5.25.

1,4-Bis[methyl(3,3,3-trifluoropropyl)silyl]benzene (26). The product was obtained in a procedure as above (47% yield): bp 105 °C (0.7 Torr); ^{1}H NMR ($CDCl_3$) δ 0.42 (d, $J = 3.6$, 6H), 1.07−1.14 (m, 4H), 2.07−2.16 (m, 4H), 4.44 (m, 2H), 7.57 (s, 4H); ^{13}C NMR ($CDCl_3$) δ −6.1, 5.4 (q, $J = 2.3$ Hz), 29.2 (q, $J = 30$ Hz), 127.5 (q, $J = 277$ Hz), 133.8, 136.4; ^{19}F NMR ($CDCl_3$) δ −69.1 (t, $J = 10.2$ Hz); IR (neat) 3052, 2965, 2907, 2128, 1442, 1365, 1266, 1210, 1129, 1069, 1030, 912, 878, 845, 829, 803 cm^{-1}. Anal. Calcd for $C_{14}H_{20}F_6Si_2$ C, 46.91; H, 5.62. Found: C, 46.57; H, 5.61.

1,4-Bis{((*E*)-2-phenylethenyl)dimethylsilyl}benzene (15a). A mixture of iodorhodium(I) tris(triphenylphosphine) (**7**, 0.1 mg, 0.1 mol %), 1,4-bis(dimethylsilyl)benzene (**14**, 0.223 mL, 1.0 mmol), and phenylethyne (**1a**, 0.220 mL, 2.0 mmol) was heated at 80 °C for 2 h with stirring. Then, the residue of the catalyst was removed by the addition of hexanes (5 mL) to form a precipitate, which was filtered off with a Celite pad. The filtrate was concentrated under reduced pressure to leave a crude oil, which was purified by column chromatography using hexanes as an eluent to yield 0.31 g of **15a** (77%): UV ($\lambda_{max} = 262$ nm, $\epsilon = 44\,400$); ^{1}H NMR ($CDCl_3$) δ 0.46 (s, 12H), 6.60 (d, $J = 19.2$ Hz, 2H), 6.98 (d, $J = 19.2$ Hz, 2H), 7.27−7.38 (m, 6H), 7.45−7.50 (m, 4H), 7.61 (s, 4H); ^{13}C NMR ($CDCl_3$) δ −2.5, 126.6, 127.1, 128.2, 128.6, 133.4, 138.2, 139.5, 145.4; IR (neat) 2957, 1605, 1574, 1495, 1447, 1379, 1248, 1132, 990, 849, 829, 801 cm^{-1}; HRMS calcd for $C_{26}H_{30}Si_2$ 398.1884, found 398.1864.

1,4-Bis{((*Z*)-2-phenylethenyl)dimethylsilyl}benzene (16a). A mixture of **7** (0.1 mg, 0.1 mol %) and **14** (0.22 mL, 1.0 mmol) in 0.1 mL of toluene was stirred at 0 °C for 1 h to give a pale yellow solution. Phenylethyne (**1a**, 0.22 mL, 2.0 mmol) was added to the solution in one portion, the solution was warmed to room temperature over a period of 2 h, and the resulting mixture was stirred at room temperature for 2 h. After the reaction was completed, 5 mL of hexanes was added to the mixture to form a precipitate, which was filtered off with a Celite pad. The filtrate was concentrated in vacuo, and the residue was purified by column chromatography using hexanes

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[26] Marciniec, B.; Walczuk-Gusciora, E.; Pietraszuk, C. *Catal. Lett.* **1998**, *55*, 125−127.

[27] Zhang, R.; Pinhas, A. R.; Mark, J. E. *Macromolecules* **1997**, *30*, 2513−2515.

as an eluent to yield 0.22 g of **16a** in 54% yield: UV (λ_{max} = 261 nm, ϵ = 20 900); ^{1}H NMR (CDCl$_3$) δ 0.26 (s, 12H), 6.00 (d, J = 15.0 Hz, 2H), 7.20−7.24 (m, 10H), 7.50 (d, J = 15.0 Hz, 2H), 7.51−7.52 (m, 4H); ^{13}C NMR (CDCl$_3$) δ −1.0, 127.5, 127.9, 128.3, 130.2, 133.1 139.7, 140.2, 148.1; IR (neat) 3407, 2959, 1592, 1570, 1493, 1445, 1381, 1250, 1132, 1072, 779 cm^{-1}; HRMS calcd for $C_{26}H_{30}Si_2$ 398.1884, found 398.1928.

General Procedure for the Preparation of (*E*)-Polymers (17−24). To a screw-capped glass tube were added RhI(PPh$_3$)$_3$ (**7**, 1.0 mg, 0.001 mmol), diethynylbenzene (1.0 mmol), and bis(dimethylsilyl)benzene (1.2 mmol) in 0.2 mL of toluene, and the resulting mixture was stirred at 60 °C. The progress of polymerization was monitored by ^{1}H NMR analysis. The resulting mixture was dissolved in 5 mL of chloroform, and the solution was poured into 100−150 mL of methanol or ethanol with vigorous stirring to form a precipitate. Filtration, washing with methanol, and drying under reduced pressure afforded the corresponding polymer. Reprecipitation was repeated twice or three times if necessary.

Poly[dimethylsilylene-*p*-phenylenedimethylsilylene-(*E*)-ethenylene-*p*-phenylene-(*E*)-ethenylene] (17). The product was obtained, after stirring at 60 °C for 1 h, as a light yellow powder: 88% yield; M_n = 20200, M_w/M_n = 5.49; T_g = 90.2 °C; UV−vis (λ_{max} = 302 nm, ϵ = 27700); Em (352 nm, Φ = 0.61%); Ex (303 nm); ^{1}H NMR (CDCl$_3$) δ 0.42 (s, 12H), 6.57 (d, J = 19.2 Hz, 2H), 6.92 (d, J = 19.2 Hz, 2H), 7.39 (br, 4H), 7.57 (br, 4H); ^{13}C NMR (CDCl$_3$) δ −2.5, 126.8, 127.3, 133.3, 138.0, 139.5, 144.9; IR (film) 2990, 2955, 1603, 1507, 1410, 1248, 1134, 985, 816 cm^{-1}.

Poly[dimethylsilylene-*m*-phenylenedimethylsilylene-(*E*)-ethenylene-*p*-phenylene-(*E*)-ethenylene] (18). The product was obtained after stirring at 60 °C for 3 h as a yellow powder: 74% yield; M_n = 10 300, M_w/M_n = 5.15; T_g = 39.2 °C; UV−vis (λ_{max} = 302 nm, ϵ = 30 100); Em (351 nm, Φ = 0.62%); Ex (303 nm); ^{1}H NMR (CDCl$_3$) δ 0.44 (s, 12H), 6.58 (d, J = 19.2 Hz, 2H), 6.93 (d, J = 19.2 Hz, 2H), 7.31−7.45 (m, 5H), 7.59 (d, J = 7.2 Hz, 2H), 7.76 (s, 1H); ^{13}C NMR (CDCl$_3$) δ −2.4, 126.8, 127.3, 127.5, 134.9, 137.8, 138.0, 139.3, 144.8; IR (film) 2957, 1603, 1507, 1410, 1364, 1105, 986, 839 cm^{-1}.

Poly[dimethylsilylene-*p*-phenylenedimethylsilylene-(*E*)-ethenylene-*m*-phenylene-(*E*)-ethenylene] (19). The product was obtained, after stirring at 100 °C for 12 h, as a yellow-green powder: 98% yield; M_n = 12 000, M_w/M_n = 3.52; T_g = 41.7 °C; UV−vis (λ_{max} = 262 nm, ϵ = 29 600); Em (361 nm, Φ = 3.30%); Ex (262 nm); ^{1}H NMR (CDCl$_3$) δ 0.43 (s, 12H), 6.60 (d, J = 19.2 Hz, 2H), 6.95 (d, J = 19.2 Hz, 2H),7.28−7.37 (m, 2H), 7.51−7.59 (m, 6H); ^{13}C NMR (CDCl$_3$) δ −2.4, 124.7, 126.4, 127.4, 128.8, 132.4, 133.3, 133.4, 138.5, 139.5, 145.2; IR (film) 3047, 2957, 1607, 1408, 1250, 1134, 987, 845 cm^{-1}.

Poly[dimethylsilylene-*m*-phenylenedimethylsilylene-(*E*)-ethenylene-*m*-phenylene-(*E*)-ethenylene] (20). The product was obtained, after stirring at 60 °C for 15 h, as a yellow-green powder: 74% yield; M_n = 11 700, M_w/M_n = 3.87; T_g = 28.7 °C; UV−vis (λ_{max} = 260 nm, ϵ = 27 600); Em (352 nm, Φ = 3.00%); Ex (262 nm); ^{1}H NMR (CDCl$_3$) δ 0.43 (s, 12H), 6.60 (d, J = 19.2 Hz, 2H), 6.93 (d, J = 19.2 Hz, 2H),7.20−7.40 (m, 4H), 7.46−7.64 (m, 4H), 7.76 (s, 2H); ^{13}C NMR (CDCl$_3$) δ −2.4, 124.8, 126.3, 127.3, 127.6, 128.8, 134.9, 137.7, 138.5, 139.3, 145.1; IR (film) 2957, 1752, 1607, 1574, 1364, 1250, 1105, 988, 839 cm^{-1}.

General Procedure for the Preparation of (*Z*)-Polymers (21−24). To a screw-capped glass tube were added toluene (0.1 mL), RhI(PPh$_3$)$_3$ (**6**, 1.0 mg, 0.001 mmol), and bis(dimethylsilyl)benzene (1.0 mmol), and the mixture was stirred at 0 °C for 1 h to form a pale brown solution, to which was added diethynylbenzene (1.0 mmol). The resulting reaction mixture was allowed to warm to room temperature over a period of 2 h, and then stirring was continued at room temperature. The progress of the polymerization was carefully monitored by ^{1}H NMR by taking an aliquot of the reaction mixture. When the monomers remained unreacted, the mixture was carefully heated to 50 °C. Purification of the polymers obtained was carried out in a similar manner by reprecipitation to the isolation of *E*-polymers. In case the precipitate turned gummy, the solvent was decanted and the residue was washed with methanol repeatedly to give the corresponding polymers.

Poly[dimethylsilylene-*p*-phenylenedimethylsilylene-(*Z*)-ethenylene-*p*-phenylene-(*Z*)-ethenylene] (21). The product was obtained, after stirring at room temperature for 18 h, as a light brown gum: 70% yield; M_n = 9400, M_w/M_n = 2.38; UV−vis (λ_{max} = 290 nm, ϵ = 15 700); Em (352 nm, Φ = 0.76%); Ex (303 nm); ^{1}H NMR (CDCl$_3$) δ 0.24 (s, 12H), 5.96 (d, J = 15.3 Hz, 2H), 7.10 (br, 4H), 7.40 (d, J = 15.3 Hz, 2H), 7.50 (br, 2H); ^{13}C NMR (CDCl$_3$) δ −1.1, 127.9, 128.6, 130.4, 133.1, 138.9, 147.7; IR (film) 2959, 1592, 1502, 1250, 1134, 819 cm^{-1}.

Poly[dimethylsilylene-*m*-phenylenedimethylsilylene-(*Z*)-ethenylene-*p*-phenylene-(*Z*)-ethenylene] (22). The product was obtained, after stirring at room temperature for 4 h, at 35 °C for 12 h, and at 50 °C for 2 h, as a brown paste: 73% yield; M_n = 8400, M_w/M_n = 2.66; UV (λ_{max} = 288 nm, ϵ = 14 500); Em (397 nm, Φ = 0.99%); Ex (303 nm); ^{1}H NMR (CDCl$_3$) δ 0.26 (s, 12H), 5.97 (d, J = 15.3 Hz, 2H), 7.10 (br, 4H), 7.25−7.64 (m, 5H), 7.76 (brs, 1H); ^{13}C NMR (CDCl$_3$) δ −0.9, 127.3, 127.9, 128.4, 130.5, 133.1, 134.3, 138.9, 147.6; IR (film) 2959, 1592, 1503, 1364, 1250, 1057, 837 cm^{-1}.

Poly[dimethylsilylene-*p*-phenylenedimethylsilylene-(*Z*)-ethenylene-*m*-phenylene-(*Z*)-ethenylene] (23). The product was obtained, after stirring at 0 °C for 2 h, at 40 °C for 12 h, and at 50 °C for 24 h, as a light brown gummy paste: 93% yield; M_n = 8500, M_w/M_n = 3.37; UV (λ_{max} = <250 nm, ϵ = 24 200); Em (352 nm, Φ = 0.93%); Ex (264 nm); ^{1}H NMR (CDCl$_3$) δ 0.24 (s, 12H), 5.98 (d, J = 15.3 Hz, 2H), 7.06 (br, 4H), 7.32−7.55 (m, 6H); ^{13}C NMR (CDCl$_3$) δ −1.1, 127.2, 127.4, 128.6, 130.6, 133.1, 139.3, 140.3, 147.8; IR (film) 2959, 2939, 1570, 1250, 1132, 872, 781 cm^{-1}.

Poly[dimethylsilylene-*m*-phenylenedimethylsilylene-(*Z*)-ethenylene-*m*-phenylene-(*Z*)-ethenylene] (24). The product was obtained, after stirring at room temperature for 2 h, at 40 °C for 12 h, and at 50 °C for 5 h, as a light brown gummy paste: 91% yield; UV (λ_{max} = <250 nm, ϵ = 25 100); Em (353 nm, Φ = 0.64%); Ex (263 nm); ^{1}H NMR (CDCl$_3$) δ 0.12 (s, 12H), 5.84 (d, J = 15.3 Hz, 2H), 6.88−6.98 (m, 5H), 7.14−7.22 (m, 2H), 7.38−7.44 (m, 2H), 7.59 (s, 1H); ^{13}C NMR (CDCl$_3$) δ −0.9, 127.2, 12.7.30, 127.35, 128.7, 130.7, 134.4, 138.8, 138.8, 138.9, 139.3, 147.7; IR (film) 2959, 1363, 1248, 1105, 881, 837, 777 cm^{-1}.

Poly[methyl(3,3,3-trifluoropropyl)silylene-*p*-phenylenemethyl(3,3,3-trifluoropropyl)silylene-(*E*)-ethenylene-*p*-phenylene-(*E*)-ethenylene] (28). To a screw-capped glass tube were added [RhI(cod)]$_2$ (**27**, 0.2 mg, 5 × 10^{-7} mol), 1,4-diethynylbenzene (**14**, 124 mg, 1.0 mmol), and 1,4-bis[methyl-(3,3,3-trifluoropropyl)silyl]benzene (**26**, 464 mg, 1.3 mmol) in 3 mL of toluene, and the resulting mixture was stirred at 80 °C for 12 h. After cooling the mixture to room temperature, toluene was removed under reduced pressure to leave a viscous liquid, which was dissolved in 0.5 mL of chloroform. The solution was poured into 500 mL of methanol with vigorous stirring. The formed precipitate was filtered, washed with methanol repeatedly, and dried under reduced pressure to afford 465 mg of colorless powder (96%): M_n = 6300, M_w/M_n = 3.72; T_g = 49 °C; UV−vis (λ_{max} = 303 nm, ϵ = 10 800); Em (395 nm, Φ = 0.11%); Ex (306 nm); ^{1}H NMR (CDCl$_3$) δ 0.48 (s, 6H), 1.13−1.17 (m, 4H), 2.07 (br, 4H), 6.54 (d, J = 19.0 Hz, 2H), 6.97 (d, J = 19.0 Hz, 2H), 7.43 (s, 4H), 7.56 (br, 4H); ^{13}C NMR (CDCl$_3$) δ −5.0, 6.3, 28.8 (q, J = 30.5 Hz), 124.1, 126.9, 127.6 (q, J = 276.5 Hz), 133.6, 146.4; ^{19}F NMR (CDCl$_3$) δ −69.0 (t, J = 10.2 Hz); IR (KBr) 2961, 1366, 1316, 1266, 1210, 1132, 1067, 1028, 988, 897, 839, 789 cm^{-1}.

Poly[methyl(3,3,3-trifluoropropyl)silylene-*m*-phenylenemethyl(3,3,3-trifluoropropyl)silylene-(*E*)-ethenylene-*p*-phenylene-(*E*)-ethenylene] (29). The reaction was carried out in a manner similar to the synthesis of **28**: yield 359 mg (74%) as a pale yellow powder; $M_n = 5600$, $M_w/M_n = 3.48$; $T_g = 28$ °C; UV−vis ($\lambda_{max} = 285$ nm, $\epsilon = 17\,900$); Em (391 nm, $\Phi = 0.15\%$); Ex (305 nm); ^{1}H NMR ($CDCl_3$) δ 0.51 (s, 6H), 1.16−1.21 (m, 4H), 2.06−2.15 (m, 4H), 6.58 (d, $J = 19.5$ Hz, 2H), 7.00 (d, $J = 19.5$ Hz, 2H), 7.45−7.75 (m, 8H); ^{13}C NMR ($CDCl_3$) δ −4.9, 6.4, 28.8 (q, $J = 30.5$ Hz), 124.2, 126.9, 127.6 (q, $J = 277.7$ Hz), 127.8, 135.4, 137.8, 139.4, 139.8, 146.4; ^{19}F NMR ($CDCl_3$) δ −69.1 (t, $J = 10.2$ Hz); IR (KBr) 2961, 1603, 1316, 1267, 1210, 1125, 1065, 1028, 988, 897, 839, 801, 781 cm^{-1}.

Poly[methyl(3,3,3-trifluoropropyl)silylene-*p*-phenylenemethyl(3,3,3-trifluoropropyl)silylene-(*E*)-ethenylene-*m*-phenylene-(*E*)-ethenylene] (30). The reaction was carried out in a manner similar to the synthesis of **28**: yield 481 mg (99%) as a pale yellow powder; $M_n = 16\,000$, $M_w/M_n = 2.12$; $T_g = 35$ °C; UV−vis ($\lambda_{max} = 253$ nm, $\epsilon = 17\,100$); Em (353 nm, $\Phi = 0.67\%$); Ex (261 nm); ^{1}H NMR ($CDCl_3$) δ 0.49 (s, 6H), 1.14−1.20 (m, 4H), 2.05−2.14 (m, 4H), 6.58 (d, $J = 19.2$ Hz, 2H), 7.01 (d, $J = 19.2$ Hz, 2H), 7.39−7.58 (m, 8H); ^{13}C NMR ($CDCl_3$) δ −5.0, 6.3, 28.8 (q, $J = 30.0$ Hz), 124.1, 126.8, 127.6 (q, $J = 276.5$ Hz), 128.9, 133.1, 133.6, 137.3, 138.0, 146.7; ^{19}F NMR ($CDCl_3$) δ −69.0 (t, $J = 10.2$ Hz); IR (KBr) 2961, 1609, 1447, 1366, 1316, 1267, 1210, 1132, 1067, 1028, 993, 897, 819, 787 cm^{-1}.

Poly[methyl(3,3,3-trifluoropropyl)silylene-*p*-phenylenemethyl(3,3,3-trifluoropropyl)silylene-(*Z*)-ethenylene-*p*-phenylene-(*Z*)-ethenylene] (32). A solution of $[RhI(cod)]_2$ (**27**, 0.2 mg, 5×10^{-7} mol) and 1,4-bis[methyl(3,3,3-trifluoropropyl)silyl]benzene (**26**, 18 mg, 0.05 mmol) in 1 mL of toluene was stirred at room temperature for 5 min. To the resulting reddish brown solution were added **26** (357 mg, 1 mmol) and 1,4-diethynylbenzene (**14**, 124 mg, 1 mmol), and stirring was continued for 3 h at room temperature. The resulting mixture was dissolved in 0.5 mL of chloroform and poured into 500 mL of methanol with vigorous stirring to form a precipitate, which was filtered off and washed with methanol. Reprecipitation was repeated twice to form 465 mg of **32** as a brown gummy paste (96%): $M_n = 6000$, $M_w/M_n = 5.39$; $T_g = 55.7$ °C; UV−vis ($\lambda_{max} = 290$ nm, $\epsilon = 33\,600$); Em (398 nm, $\Phi = 0.16\%$); Ex (306 nm); ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 6H), 0.93−0.98 (m, 4H), 1.86 (br, 4H), 5.93 (d, $J = 15.0$ Hz, 2H), 7.05 (s, 2H), 7.47−7.52 (m, 6H); ^{13}C NMR ($CDCl_3$) δ −3.9, 7.6, 28.6 (q, $J = 30.0$ Hz), 127.0, 127.5 (q, $J = 276.3$ Hz), 128.9, 133.4, 138.1, 138.8, 149.4; ^{19}F NMR ($CDCl_3$) δ −69.1 (t, $J = 10.2$ Hz); IR (KBr) 2967, 1593, 1366, 1316, 1266, 1210, 1180, 1067, 1028, 993, 897, 839, 787 cm^{-1}.

Poly[methyl(3,3,3-trifluoropropyl)silylene-*m*-phenylene-methyl(3,3,3-trifluoropropyl)silylene-(*Z*)-ethenylene-*p*-phenylene-(*Z*)-ethenylene] (33). The reaction was carried out in a manner similar to that described in the synthesis of **32** to afford 315 mg of gummy brown **33** in 65% yield after stirring at 80 °C for 5 h: $M_n = 7300$, $M_w/M_n = 3.15$; $T_g = 23.4$ °C; UV−vis ($\lambda_{max} = 302$ nm, $\epsilon = 24\,300$); Em (394 nm, $\Phi = 0.66\%$); Ex (305 nm); ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 6H), 0.92−0.96 (m, 4H), 1.81−1.91 (m, 4H), 5.91 (d, $J = 14.7$ Hz, 2H), 7.00 (br, 4H), 7.37−7.50 (m, 6H); ^{13}C NMR ($CDCl_3$) δ −4.0, 7.5, 28.6 (q, $J = 30.0$ Hz), 127.2, 127.5 (q, $J = 277.0$ Hz), 127.6, 128.3, 133.0, 133.4, 138.0, 139.0, 149.4; ^{19}F NMR ($CDCl_3$) δ −69.4 (t, $J = 10.2$ Hz); IR (KBr) 2965, 1480, b1447, 1366, 1316, 1266, 1210, 1129, 1067, 1028, 897, 839, 785 cm^{-1}.

Poly[methyl(3,3,3-trifluoropropyl)silylene-*p*-phenylenemethyl(3,3,3-trifluoropropyl)silylene-(*Z*)-ethenylene-*m*-phenylene-(*Z*)-ethenylene] (34). The reaction was carried out in a manner similar to that described in the synthesis of **32** to afford 315 mg of gummy brown **34** in 65% yield after stirring at room temperature for 3 h: $M_n = 9300$, $M_w/M_n = 6.40$; $T_g = 34.5$ °C; UV−vis ($\lambda_{max} = 261$ nm, $\epsilon = 25\,100$); Em (356 nm, $\Phi = 1.37\%$); Ex (262 nm); ^{1}H NMR ($CDCl_3$) δ 0.21 (s, 6H), 0.91−0.97 (m, 4H), 1.81−1.90 (m, 4H), 5.90 (d, $J = 15.0$ Hz, 2H), 7.01 (s, 4H), 7.30−7.61 (m, 6H); ^{13}C NMR ($CDCl_3$) δ −3.8, 7.6, 28.6 (q, $J = 29.4$ Hz), 126.2, 127.0 127.5 (q, $J = 268.5$ Hz), 127.7, 134.9, 136.3, 138.7, 139.2, 149.3; ^{19}F NMR ($CDCl_3$) δ −69.1 (t, $J = 10.2$ Hz); IR (KBr) 2965, 1364, 1316, 1266, 1210, 1125, 1067, 1028, 897, 839, 800, 708 cm^{-1}.

Poly[methyl(3,3,3-trifluoropropyl)silylene-*m*-phenylenemethyl(3,3,3-trifluoropropyl)silylene-(*Z*)-ethenylene-*m*-phenylene-(*Z*)-ethenylene] (35). The reaction was carried out in a manner similar to that described in the synthesis of **32** to afford 295 mg of gummy brown **35** in 61% yield after stirring at 80 °C for 6 h: $M_n = 15\,400$, $M_w/M_n = 3.80$; $T_g = 9.5$ °C; UV−vis ($\lambda_{max} = 259$ nm, $\epsilon = 26\,100$); Em (354 nm, $\Phi = 0.89\%$); Ex (268 nm); ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 6H), 0.88−0.94 (m, 4H), 1.82−1.85 (m, 4H), 5.89 (d, $J = 15.3$ Hz, 2H), 6.97 (brs, 4H), 7.31−7.57 (m, 6H); ^{13}C NMR ($CDCl_3$) δ −3.9, 7.6, 28.6 (q, $J = 30.0$ Hz), 127.2, 127.5 (q, $J = 268.5$ Hz), 127.5, 127.7, 128.1, 128.3, 133.8, 134.9, 136.3, 138.9, 149.3; ^{19}F NMR ($CDCl_3$) δ −69.1 (t, $J = 10.2$ Hz); IR (KBr) 2967, 1366, 1316, 1266, 1210, 1125, 1067, 1028, 897, 839, 804, 706 cm^{-1}.

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Supporting Information Available: NMR and emission spectra of polymers **17**−**24** and **28**−**35**. This material is available free of charge via the Internet at http://pubs.acs.org.

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