Cationic Rhodium Complex-Catalyzed Highly Selective Dehydrogenative Silylation of Styrene

Ryo Takeuchi* and Hiroyuki Yasue

Department of Environmental Science, Faculty of Science, Yokohama City University, Kanazawa-Ku, Yokohama 236, Japan

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Cationic rhodium complex-catalyzed dehydrogenative silylation of styrene with hydrosilanes was studied. Dehydrogenative silylation was competitive with hydrosilylation. The selectivity was strongly dependent on the reaction temperature and the molar ratio of styrene to hydrosilane. The selectivity of dehydrogenative silylation was 92% when using 3 equiv of styrene to 1 equiv of triethylsilane (**1a**) in refluxing diethyl ketone. The nature of the hydrosilane also affected the reaction. As the steric bulk of hydrosilane increased, the selectivity of dehydrogenative silylation increased. Dehydrogenative silylation product (**2d**) was obtained exclusively in 81% yield when using triisopropylsilane (**1d**). The amount of ligand had a large influence on the selectivity of the reaction. As the amount of PPh_3 used increased, the selectivity of dehydrogenative silylation increased. These results were reasonably explained according to the mechanism involving the insertion of styrene into the rhodium−silicon bond which was formed by the oxidative addition of hydrosilane to rhodium complex.

Introduction

Dehydrogenative silylation of organic compounds with hydrosilanes is a useful method for the synthesis of organosilicon compounds.[1] The process is effectively catalyzed by transition metal complexes. Whereas dehydrogenative silylation of alcohols with hydrosilanes is well studied,[2] dehydrogenative silylation of alkenes with hydrosilanes[3] is relatively unexplored. From a synthetic point of view, the reaction is important because the product is a vinylsilane.[4] Dehydrogenative silylation of alkenes is attractive as a useful alternative to hydrosilylation of alkynes,[5] a reaction in which there are regio- and stereochemical problems. The major drawback of dehydrogenative silylation of alkenes is that it is always competitive with hydrosilylation of the alkenes under the reaction conditions. The reaction gives a mixture of the dehydrogenative silylation product and the hydrosilylation product. A highly selective process thus is desired. Recently, Murai and co-workers have developed highly selective dehydrogenative silylation of alkenes catalyzed by transition metal complexes.[6]

Rhodium complexes have been known to be an efficient catalyst for hydrosilylation of alkenes.[7] Several examples of *neutral* rhodium complex-catalyzed dehydrogenative silylation of alkenes have been reported.[6a,8] However, in these examples there was competitive hydrosilylation of the alkenes,[9] so the selectivity of dehydrogenative silylation is not satisfactory. Previously, we reported that a *cationic* rhodium complex was an efficient catalyst for highly regio- and stereoselective

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(1) Corey, J. Y. *Adv. Silicon Chem.* **1991**, *1*, 327.

(2) For a review, see: Lukevics, E.; Dzintara, M. *J. Organomet. Chem.* **1985**, *295*, 265. For recent works, see: (a) Gregg, B. T.; Culter, A. R. *Organometallics* **1994**, *13*, 1039. (b) Doyle, M. P.; High, K. G.; Baghari, V. B.; Pieters, R. J.; Lewis, P. J.; Pearson, M. M. *J. Org. Chem.* **1990**, *55*, 6082. (c) Luo, X-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527.

(3) (a) Christ, M. L.; Sabo-Etinne, S.; Chaudret, B. *Organometallics* **1995**, *14*, 1082. (b) Corey, J. Y.; Xiano-Hong, Z. *Organometallics* **1992**, *11*, 672. (c) Kesti, M. R.; Waymouth, R. M. *Organometallics* **1992**, *11*, 1095. (c) Tanke, R. S.; Crabtree, R. H. *Organometallics* **1991**, *10*, 415. (d) Kesti, M. R.; Abdulrahman, M.; Waymouth, R. M. *J. Organomet. Chem.* **1991**, *417*, C12. (e) Marciniec, B.; Maciejewski, H.; Mirecki, J. *J. Organomet. Chem.* **1991**, *418*, 61. (f) Skoda-Foldes, R.; Kollar, L.; Heil, B. *J. Organomet. Chem.* **1991**, *408*, 297. (g) Skoda-Foldes, R.; Kollar, L.; Heil, B. *J. Organomet. Chem.* **1989**, *366*, 275. (h) Hori, Y.; Mitsudo, T.; Watanabe, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3011. (i) Fernandez, M. J.; Esteruelas, M. A.; Jimenez, M. S.; Oro, L. A. *Organometallics* **1986**, *5*, 1519. (j) Marciniec, B.; Gulinski, J. *J. Organomet. Chem.* **1983**, *253*, 349. (k) Schroeder, M.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345. (l) Nesyanov, A. N.; Freidlina, R. K.; Chukovskaya, E. C.; Petrova, R. G.; Belyavsky, A. B. *Tetrahedron* **1962**, *17*, 61.

(4) (a) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375. (b) Fleming, I.; Dunogues, J.; Smithers, R. H. *Org. React.* **1989**, *37*, 57. (c) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988; p 7. (d) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983; p 79. (e) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981; p 44.

(5) For a review, see: (a) Marciniec, B. *Comprehensive Handbook on Hydrosilylation*; Pergamon Press: Oxford, U.K., 1992; p 130. (b) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 8, p 769. (c) Ojima, I. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1480.

(6) (a) Kakiuchi, F.; Nogami, K.; Chatani, N.; Seki, Y.; Murai, S. *Organometallics* **1993**, *12*, 4748. (b) Kakiuchi, F.; Tanaka, Y.; Chatani, N.; Murai, S. *J. Organomet. Chem.* **1993**, *456*, 45. (c) Takeshita, K.; Seki, Y.; Kawamoto, K.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1987**, *52*, 4864. (d) Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1986**, *51*, 3890. (e) Takeshita, K.; Seki, Y.; Kawamoto, K.; Murai, S.; Sonoda, N. *J. Chem. Soc., Chem. Commun.* **1983**, 1193. (f) Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 928.

(7) (a) Murai, T.; Oda, T.; Kimura, F.; Onishi, H.; Kanda, T.; Kato, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2143. (b) Tamao, K.; Nakagawa, Y.; Ito, Y. *Organometallics* **1993**, *12*, 2297. (c) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2121. (d) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2128. (e) Chance, J.; Nile, T. A. *J. Mol. Catal.* **1987**, *42*, 91. (f) Brockmann, M.; Dieck, H.; Klaus, J. *J. Organomet. Chem.* **1986**, *301*, 209. (g) Cornish, A. J.; Lappert, M. F. *J. Organomet. Chem.* **1984**, *271*, 153. (h) Dickers, H. M.; Haszeldine, R. N.; Malkin, L. S.; Mather, A. P.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1980**, 308. (i) Cornish, A.; Lappert, M. F.; Filatovs, G. L.; Nile, T. A. *J. Organomet. Chem.* **1979**, *172*, 153. (j) Hill, J. E.; Nile, T. A. *J. Organomet. Chem.* **1977**, *137*, 293. (k) Hazeldine, R. N., Parish, R. V.; Parry, D. J. *J. Chem. Soc. A* **1969**, 683. (l) Charentenay, F.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 787.

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Table 1. Effect of Molar Ratio on Cationic Rhodium Complex-Catalyzed Dehydrogenative Silylation of Styrene with Triethylsilane (1a)[a]

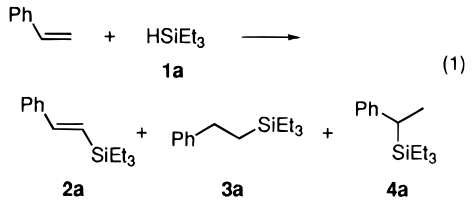
entry	$HSiEt_3$ **1a**/mmol	styrene/mmol	yield/%[b]	product distributn[b] **2a:3a:4a**
1	2	6	92	92:8:0
2	2	20	92	92:8:0
3	3	2	53	58:42:0
4	6	2	55	58:42:0

[a] A mixture of styrene, $HSiEt_3$, $[Rh(COD)_2]BF_4$ (0.02 mmol), PPh_3 (0.04 mmol), and diethyl ketone (3 mL) was stirred under reflux for 1 h. [b] Determined by GLC.

hydrosilylation of 1-alkynes.[10] We first disclosed that the stereoselectivity of *cationic* rhodium complex-catalyzed hydrosilylation of 1-alkynes was completely opposite to that catalyzed by a *neutral* counterpart such as $RhCl(PPh_3)_3$. These findings prompted us to study *cationic* rhodium complex-catalyzed dehydrogenative silylation of alkenes. We report here a systematic study of *cationic* rhodium complex-catalyzed dehydrogenative silylation of styrene.

Results and Discussion

The reaction of styrene with triethylsilane (**1a**) in the presence of a catalytic amount of $[Rh(COD)_2]BF_4/2PPh_3$ in refluxing diethyl ketone gave (*E*)-1-phenyl-2-(triethylsilyl)ethene (**2a**, dehydrogenative silylation product) and 1-phenyl-2-(triethylsilyl)ethane (**3a**, hydrosilylation product) (eq 1). 1-Phenyl-1-(triethylsilyl)ethane (**4a**,



hydrosilylation product) was not formed. Ethylbenzene formed by hydrogenation of styrene, was also obtained in an amount equal to that of **2a**. The result clearly shows styrene acts as a hydrogen acceptor. Dehydrogenative silylation was competitive with hydrosilylation. Thus, we have focused on developing a highly selective dehydrogenative silylation. We found that the ratio of styrene to triethylsilane affected markedly the selectivity of dehydrogenative silylation. Results are summarized in Table 1. The use of an excess of styrene relative to triethylsilane increased the selectivity of dehydrogenative silylation, whereas the selectivity of hydrosilylation decreased. Dehydrogenative silylation product **2a** was obtained in 92% selectivity when using 3 equiv of styrene to 1 equiv of triethylsilane (entry 1). Using 10 equiv of styrene to 1 equiv of triethylsilane did not improve the selectivity of dehydrogenative silylation (entry 2). When 1.5 equiv of triethylsilane to 1 equiv of styrene was used in refluxing diethyl ketone, the selectivity of dehydrogenative silylation was decreased to 58% (entry 3). Hydrosilylation product **3a** was obtained in 42% selectivity. It is apparent that an excess of styrene is essential for selective dehydrogenative silylation. Diethyl ketone was used as solvent throughout these reactions. Although a cationic rhodium complex can catalyze hydrosilylation of ketones,[11] diethyl ketone was not hydrosilylated under the reaction conditions.

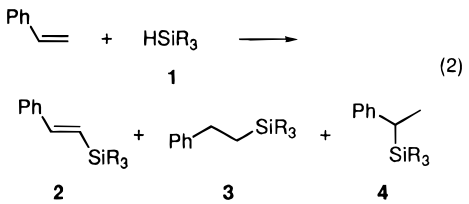
Table 2. Effect of Temperature on Cationic Rhodium Complex-Catalyzed Dehydrogenative Silylation of Styrene with Triethylsilane (1a)[a]

entry	conditions	yield/%[b]	product distributn[b] **2a:3a:4a**
1	reflux, 1 h	92	92 8 0
2	70 °C, 1 h	92	87 13 0
3	50 °C, 2 h	91	78 22 0
4	room temp, 18 h	19	17 83 0

[a] A mixture of styrene (6 mmol), $HSiEt_3$ (2 mmol), $[Rh(COD)_2]BF_4$ (0.02 mmol), PPh_3 (0.04 mmol), and diethyl ketone (3 mL) was stirred. [b] Determined by GLC.

The selectivity was highly sensitive to the reaction temperature (Table 2). As the reaction temperature increased, the selectivity of dehydrogenative silylation increased. Each reaction had to be initiated exactly at the recorded temperature. At room temperature the selectivity of dehydrogenative silylation was 17%. Hydrosilylation took place predominantly over dehydrogenative silylation (entry 4). The reaction in refluxing diethyl ketone gave the dehydrogenative silylation product in 92% selectivity (entry 1). Maitlis and coworkers reported the opposite temperature dependence. In the $[Cp^*RhCl_2]_2$-catalyzed reaction of 1-hexene with triethylsilane, the selectivity of dehydrogenative silylation decreased as temperature increased.[8c]

It is well-known that the reactivity of the Si−H bond is greatly influenced by substituents on the silicon atom and they also affect the selectivity in hydrosilylation, e.g., chemo-, regio-, and stereoselectivity.[12] Various hydrosilanes could be used in the reaction with styrene (eq 2). Results are summarized in Table 3. The



reaction was carried out at 50 °C to eliminate the effect of temperature. The selectivity of the reaction was strongly dependent on the nature of the hydrosilane used. Dehydrogenative silylation occurred predominantly over hydrosilylation in the reactions of triethylsilane (**1a**) and tri-*n*-propylsilane (**1c**), relatively bulky hydrosilanes (entries 1 and 3). As the steric bulk of hydrosilane increased, the selectivity of dehydrogenative silylation increased. The reaction with *tert*-butyldimethylsilane (**1e**) gave a dehydrogenative silylation prod-

(8) (a) Doyle, M. P.; Devora, G. A.; Nefedov, A. O.; High, K. G. *Organometallics* **1992**, *11*, 549. (b) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90. (c) Millan, A.; Fernandez, M.-J.; Bentz, P.; Maitlis, P. M. *J. Mol. Catal.* **1984**, *26*, 89. (d) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1984**, *49*, 3389. (e) Ojima, I.; Fuchikami, T.; Yatabe, M. *J. Organomet. Chem.* **1984**, *260*, 335. (f) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1983**, *48*, 5101. (g) Kuncova, G.; Chvalovsky, V. *Collect. Czech. Chem. Commun.* **1980**, *45*, 2240.

(9) Highly selective dehydrogenative silylation is limitted to the reaction of 1,5-dienes; see ref 6a.

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

(11) (a) Hayashi, T.; Yamamoto, K.; Kasuga, K.; Omizu, H.; Kumada, M. *J. Organomet. Chem.* **1976**, *113*, 127. (b) Hayashi, T.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1973**, *54*, C45.

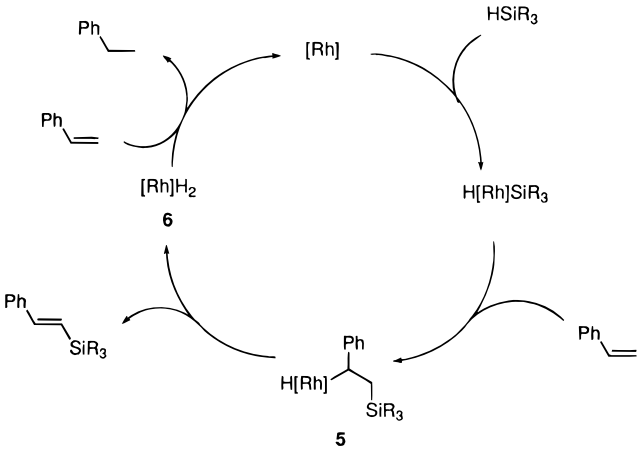
(12) Marciniec, B. *Comprehensive Handbook on Hydrosilylation*; Pergamon Press: Oxford, U.K., 1992; p 160.

Table 3. Effect of Hydrosilane on Cationic Rhodium Complex-Catalyzed Dehydrogenative Silylation of Styrene[a]

entry	hydrosilane	time/h	yield/%[b]	product distributn[c] **2:3:4**
1	$HSiEt_3$ (**1a**)	2	91	78 22 0
2	$HSiEt_2Me$ (**1b**)	2	83	51 49 0
3	$HSi(n\text{-}Pr)_3$ (**1c**)	2	90	84 16 0
4[d]	$HSi(i\text{-}Pr)_3$ (**1d**)	64	81	100 0 0
5[d]	$HSi(t\text{-}Bu)Me_2$ (**1e**)	15	85	95 5 0
6	$HSiPhMe_2$ (**1f**)	2	88	12 88 0
7[e]	$HSi(OEt)_3$ (**1g**)	3	67	26 74 0

[a] A mixture of styrene (6 mmol), $HSiR_3$ (2 mmol), $[Rh(COD)_2]BF_4$ (0.02 mmol), PPh_3 (0.04 mmol), and diethyl ketone (3 mL) was stirred under at 50 °C. [b] Isolated yield. [c] Determined by GLC. [d] 1,2-Dichloroethane (3 mL). [e] Under refluxing 1,2-dichloropropane (3 mL).

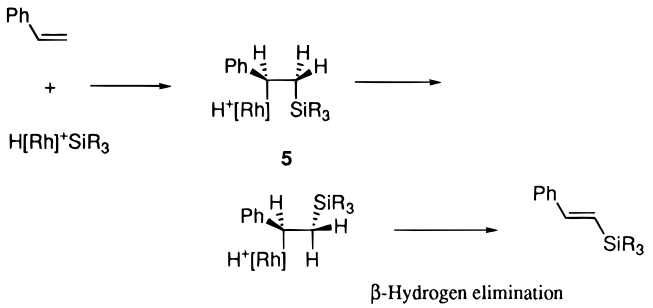
Scheme 1



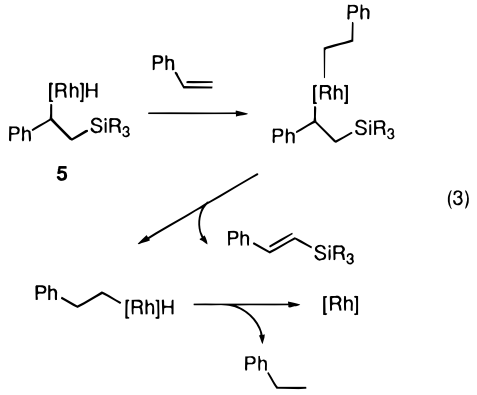
uct (**2e**) in 95% selectivity (entry 5). The reaction with triisopropylsilane (**1d**) gave a dehydrogenative silylation product (**2d**) exclusively and required 64 h for its completion (entry 4). $RhCl(PPh_3)_3$-catalyzed reaction of styrene with triisopropylsilane (**1d**) was reported to give **2d** in 30% yield.[8f] Cationic complex-catalyzed reactions gave a superior result than neutral complex-catalyzed reaction. The reaction has special synthetic value because vinyltriisopropylsilane is a useful synthetic intermediate.[13] In contrast, the reaction with diethylmethylsilane (**1b**), a less bulky hydrosilane than **1a**, gave equal amounts of dehydrogenative silylation (**2b**) and hydrosilylation (**3b**) products (entry 2). Hydrosilylation occurred predominantly vs dehydrogenative silylation with dimethyphenylsilane (**1f**) and triethoxysilane (**1g**) (entries 6 and 7). Tamao and co-workers also reported that 8-methoxynaphthyldimethylsilane, a bulky aryldimethylsilane, was effective for $RhCl(PPh_3)_3$-catalyzed highly selective dehydrogenative silylation of styrene.[14]

The mechanism of dehydrogenative silylation of styrene has been proposed to involve silylmetalation.[3c,e,k,6c,d,8b−f] A possible mechanism is outlined in Scheme 1. The insertion of styrene into the silicon−rhodium bond, which is generated by the oxidative addition of hydrosilane to rhodium, gives complex **5**. β-Hydrogen elimination then gives **2** and rhodium dihydride complex (**6**). Hydrogenation of styrene regenerates a catalytically active rhodium species. The

Scheme 2



possibility of a dialkylrhodium complex cannot be ruled out (eq 3). Highly selective dehydrogenative silylation



using a bulky trialkylsilane is reasonably explained with the silylmetalation mechanism. Silylrhodation proceeds in a syn-manner.[15] When the silyl group is bulky, the steric repulsion between the silyl group and the cationic rhodium moiety is serious. To relieve the steric repulsion, a bond rotation of about 120° brings a hydrogen into the syn periplanar relationship with the cationic rhodium moiety. The syn periplanar Rh−H arrangement[16] induces β-hydrogen elimination giving a dehydrogenative silylation product (Scheme 2).

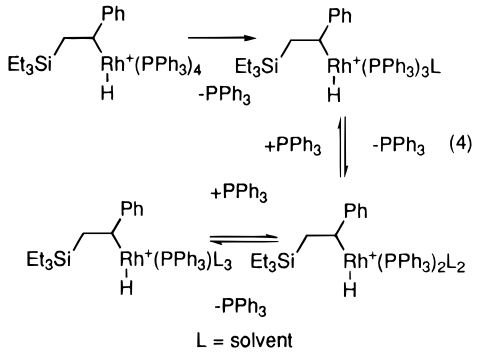
The effect of the phosphorus ligand on the rhodium-catalyzed dehydrogenative silylation of styrene has not been previously examined. We have examined the effect of mono- and bidentate phosphorus ligands. Results are summarized in Table 4. The amount of ligand had a great influence on the selectivity of the reaction. As the amount of PPh_3 used increased, the selectivity of dehydrogenative silylation increased at the expense of the reaction rate. For example, the selectivity was raised to 97% when using 10 equiv of PPh_3 to 1 equiv of Rh, but the reaction required 18 h for completion (entry 5). The effect of the amount of PPh_3 is explained reasonably according to Scheme 2 and eq 4. The presence of additional PPh_3 causes the equilibrium shown in eq 4 to shift to a cationic rhodium species coordinated by a greater number of PPh_3 groups. The resulting cationic rhodium species suffers from serious steric repulsion between the triethylsilyl group and the cationic rhodium−phosphine moiety. A bond rotation of about 120° will relieve the steric repulsion to give the syn periplan-

(13) Rucker, C. *Chem. Rev.* **1995**, *95*, 1009.
(14) Kimae, Y.; Tamao, K.; Nakagawa, Y.; Seshimoto, H.; Ito, Y. *Abstracts of the 10th International Symposium on Organosilicon Chemistry*; Poznań, Poland, 1993, P-65.
(15) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127.
(16) The syn periplanar relationship of M−C−C−H is required for β-hydrogen elimination; see: (a) Crabtree, R. H. *The Organometallic Chemistry of The Transition Metals*; John Wiley & Sons: New York, 1994; p 174. (b) McDermott, J. X.; White, J. F.; Whitesides G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.

Table 4. Effect of Ligand on Cationic Rhodium Complex-Catalyzed Dehydrogenative Silylation of Styrene with Triethylsilane (1a)[a]

entry	ligand	P/Rh	time/h	yield/%[b]	product distributn[b] **2a:3a:4a**
1[c]		0	1	65	80 20 0
2	PPh_3	2	2	91	78 22 0
3	PPh_3	4	5	80	92 8 0
4	PPh_3	6	7	76	95 5 0
5	PPh_3	10	18	72	97 3 0
6	$PPh_2(C_6F_5)$	2	1	86	90 10 0
7	$PPh_2(C_6F_5)$	4	3	85	93 7 0
8[d]	$PPh_2(C_6F_5)$	10	14	86	96 4 0
9[d]	PPh_2Me	2	16	86	52 48 0
10	$P(n\text{-}Bu)_3$	2	6	81	42 58 0
11[d]	$P(OEt)_3$	2	6	88	47 53 0
12[d]	$P(OPh)_3$	2	8	80	15 73 12
13	dppe	2	5	88	62 20 18
14	dppp	2	24	88	78 17 5
15	dppb	2	22	91	77 22 1
16	dppf	2	25	86	77 20 3

[a] A mixture of styrene (6 mmol), $HSiEt_3$ (2 mmol), $[Rh(COD)_2]BF_4$ (0.02 mmol), ligand, and diethyl ketone (3 mL) was stirred under at 50 °C. [b] Determined by GLC. [c] Acetone (3 mL). [d] 1,2-Dichloroethane (3 mL).



er Rh−H arrangement. Thus, dehydrogenative silylation can easily occur.

The electronic nature of ligand also is important. $PPh_2(C_6F_5)$ was found to be a more effective ligand for the dehydrogenative silylation than PPh_3. The selectivity of dehydrogenative dehydrogenative silylation was 90% when using 2 equiv of $PPh_2(C_6F_5)$ to 1 equiv of Rh (entry 6). An excess of $PPh_2(C_6F_5)$ to Rh increased the selectivity of dehydrogenative silylation as observed for PPh_3 (entries 7 and 8). The increased elecron deficiency of the metal center increased the selectivity of dehydrogenative silylation vs hydrosilylation. On the other hand, the reactions in which more electron-donating phosphine ligands such as PPh_2Me and $P(n\text{-}Bu)_3$ were used gave nearly equal amounts of hydrosilylation and dehydrogenative silylation products (entries 9 and 10). With bidentate ligands, dehydrogenative silylation took place predominantly over hydrosilylation. The reactions gave a product distribution similar to that observed with PPh_3 (entries 13−16).

In conclusion, a cationic rhodium complex is an efficient catalyst for the reaction of styrene with a hydrosilane. The reaction was selective for the dehydrogenative silylation when an excess of styrene relative to the hydrosilane is used.

Experimental Section

Materials. All reagents were dried and purified before use by the usual procedures. $[Rh(COD)_2]BF_4$ was prepared by literature method.[17] Styrene and hydrosilanes were purchased.

General Methods. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL-EX-270 spectrometer. Samples were dissolved in $CDCl_3$ solutions, and the chemical shift values were expressed relative to Me_4Si as an internal standard. GC analyses were performed on a Shimadzu GC-14A with 3-mm × 2-m glass columns packed with either 20% SE-30 on 60/80 mesh chromosorb w, AW-DMCS, or 5% OV-17 on 60/80 mesh chromosorb w, AW-DMCS. GC−MS spectra were recorded on a Shimadzu QP-2000 spectrometer. Column chromatography was carried out on 70−230 mesh silica gel (Merk; Silica Gel 60). Elemental analyses were performed at the Microanalytical Center of Kyoto University.

General Procedure for the Dehydrogenative Silylation of Styrene. A two-necked flask equipped with a magnetic stirring bar was charged with $[Rh(COD)_2]BF_4$ (8.1 mg, 0.02 mmol) and PPh_3 (10.5 mg, 0.04 mmol) . The reactor was evacuated and filled with argon. Solvent (3 mL) was added to the flask. The mixture was stirred in 5 min. Styrene (6 mmol) was added via a syringe, followed by similar addition of hydrosilane (2 mmol). The reactor was immediately immersed in an oil bath which was kept at the required reaction temperature. The mixture was stirred under the conditions shown in the tables. The progress of the reaction was monitored by GLC. After the reaction was completed, the solution was concentrated in vacuo. The products were isolated by column chromatography. Samples were purified by a preparative gas chromatography.

(*E*)-1-(Triethylsilyl)-2-phenylethene (2a):[6d,8f,10] ^1H NMR δ 0.66 (q, 6H, J = 7.9 Hz), 0.99 (t, 9H, J = 7.9 Hz), 6.42 (d, 1H, J = 19.5 Hz), 6.89 (d, 1H, J = 19.5 Hz), 7.18−7.44 (m, 5H); ^{13}C NMR δ 3.5, 7.4, 125.9, 126.3, 127.9, 128.5, 138.5, 144.9.

1-(Triethylsilyl)-2-phenylethane (3a):[8f] ^1H NMR δ 0.55 (q, 6H, J = 7.9 Hz), 0.85−0.92 (m, 2H), 0.96 (t, 9H, J = 7.9 Hz), 2.58−2.64 (m, 2H), 7.15−7.44 (m, 5H); ^{13}C NMR δ 3.3, 7.4, 13.7, 30.1, 125.5, 127.7, 128.3, 145.6.

1-(Triethylsilyl)-1-phenylethane (4a):[3fg,8af,18] ^1H NMR δ 0.51 (q, 6H, J = 7.9 Hz), 0.80 (t, 9H, J = 7.9 Hz), 1.37 (d, 3H, J = 7.6 Hz), 2.30 (q, 1H, J = 7.6 Hz), 7.05−7.28 (m, 5H); ^{13}C NMR δ 2.1, 7.4, 15.4, 26.8, 124.2, 127.1, 128.0, 146.3. Anal. Calcd for $C_{14}H_{24}Si$: C, 76.29; H, 10.97; Si, 12.74. Found: C, 76.49; H, 11.16.

(*E*)-1-(Diethylmethylsilyl)-2-phenylethene (2b):[6d] ^1H NMR δ −0.11 (s, 3H), 0.53 (q, 4H, J = 7.9 Hz), 0.87 (t, 6H, J = 7.9 Hz), 6.33 (d, 1H, J = 19.5 Hz), 6.78 (d, 1H, J = 19.5 Hz), 7.03−7.33 (m, 5H); ^{13}C NMR δ −6.0, 5.5, 7.4. 126.3, 127.0, 127.9, 128.5, 138.4, 144.5.

1-(Diethylmethylsilyl)-2-phenylethane (3b):[19] ^1H NMR δ −0.15 (s, 3H), 0.41 (q, 4H, J = 7.9 Hz), 0.73−0.80 (m, 2H), 0.83 (t, 6H, J = 7.9 Hz), 2.46−2.53 (m, 2H), 7.00−7.33 (m, 5H); ^{13}C NMR δ −6.3, 5.0, 7.4, 15.2, 30.0, 125.4, 127.7, 128.3, 145.4.

(*E*)-1-(Tri-*n*-propylsilyl)-2-phenylethene (2c): ^1H NMR δ 0.63−0.69 (m, 6H), 0.98 (t, 9H, J = 7.3 Hz), 1.32−1.43 (m, 6H), 6.43 (d, 1H, J = 19.5 Hz), 6.87 (d, 1H, J = 19.5 Hz), 7.18−7.45 (m, 5H); ^{13}C NMR δ 15.4, 17.5, 18.6, 126.3, 127.0, 127.8, 128.5, 138.5, 144.4; MS (*m*/*e*, %) 260 (M^+, 1.6), 219 (10.7), 218 (49.1), 217 (38.8), 176 (21.9), 175 (100.0), 147 (5.7), 133 (84.9), 131 (55.7), 107 (13.3). Anal. Calcd for $C_{17}H_{28}Si$: C, 78.39; H, 10.83; Si, 10.78. Found: C, 78.18; H, 10.97.

1-(Tri-*n*-propylsilyl)-2-phenylethane (3c):[20] ^1H NMR δ 0.51−0.58 (m, 6H), 0.84−0.92 (m, 2H), 0.95 (t, 9H, J = 7.3

(17) Schenck, T. G.; Downs, J. M.; Milne, C. R. C.; Mackenzie, P.; Boucher, H.; Whealan, J.; Bosnich, B. *Inorg. Chem.* **1985**, *24*, 2334.
(18) (a) Donskaya, N. A.; Yureva N. M.; Voevodskaya, T. I.; Sigeev, A. S.; Beletskaya, I. P. *Russ. J. Org. Chem.* **1994**, *30*, 801. (b) Lewis, L. N.; Uriarte, R. J.; Lewis, N. *J. Catal.* **1991**, *127*, 67. (c) Caseri, W.; Pregosin P. S. *J. Organomet Chem.* **1988**, *356*, 259. (d) Albinati, A.; Caseri, W. R.; Pregosin P. S. *Organometallics* **1987**, *6*, 788.
(19) Caseri, W.; Pregosin, P. S. *Organometallics* **1988**, *7*, 1373.
(20) El-Durini, N. M. K.; Jackson, R. A. *J. Organomet. Chem.* **1982**, *232*, 117.

Hz), 1.30−1.46 (m, 6H), 2.57−2.63 (m, 2H), 7.14−7.44 (m, 5H); ^{13}C NMR δ 14.9, 15.2, 17.5, 18.6, 30.1, 125.4, 127.7, 128.3, 145.6.

(*E*)-1-(Triisopropylsilyl)-2-phenylethene (2d):[8f] ^{1}H NMR δ 1.07−1.22 (m, 21H), 6.40 (d, 1H, J = 19.5 Hz), 6.94 (d, 1H, J = 19.5 Hz), 7.20−7.46 (m, 5H); ^{13}C NMR δ 11.0, 18.7, 123.9, 126.3, 127.8, 128.5, 138.7, 145.6.

(*E*)-1-(*tert*-Butyldimethylsilyl)-2-phenylethene (2e): ^{1}H NMR δ 0.12 (s, 6H), 0.92 (s, 9H), 6.48 (d, 1H, J = 19.1 Hz), 6.89 (d, 1H, J = 19.1 Hz), 7.20−7.45 (m, 5H); ^{13}C NMR δ −6.0, 16.8, 26.5. 126.4, 126.7, 127.9, 128.5, 138.4, 144.9; MS (*m*/*e*, %) 218 (M^+, 1.4), 161 (100.0), 145 (46.4), 135 (21.0), 121 (2.2). Anal. Calcd for $C_{14}H_{22}Si$: C, 76.99; H, 10.15; Si, 12.86. Found: C, 77.12; H, 10.41.

1-(*tert*-Butyldimethylsilyl)-2-phenylethane (3e): ^{1}H NMR δ 0.02 (s, 6H), 0.89−0.95 (m, 11H), 2.60−2.68 (m, 2H), 7.20−7.46 (m, 5H); ^{13}C NMR δ −6.4, 14.8, 16.6, 26.6, 30.4, 125.5, 127.7, 128.3, 145.5; MS (*m*/*e*, %) 220 (M^+, 3.5), 164 (18.2). 163 (100.0), 148 (3.7), 145 (4.1). Anal. Calcd for $C_{14}H_{24}Si$: C, 76.29; H, 10.97; Si, 12.74. Found: C, 76.26; H, 11.25.

(*E*)-1-(Dimethylphenylsilyl)-2-phenylethene (2f):[6d] ^{1}H NMR δ 0.43 (s, 6H), 6.58 (d, 1H, J = 19.1 Hz), 6.94 (d, 1H, J = 19.1 Hz), 7.15−7.54 (m, 10H); ^{13}C NMR δ −2.5, 126.5, 127.1, 128.1, 128.5, 129.0, 133.9, 138.2, 138.5, 139.8, 145.3.

1-(Dimethylphenylsilyl)-2-phenylethane (3f):[21] ^{1}H NMR δ 0.28 (s, 6H), 1.08−1.15 (m, 2H), 2.59−2.65 (m, 2H), 7.12−7.55 (m, 10H); ^{13}C NMR δ −3.1, 17.7, 29.9, 125.5, 127.75, 127.78, 128.3, 128.9, 133.6, 139.0, 144.9.

(*E*)-1-(Triethoxysilyl)-2-phenylethene (2g):[6d] ^{1}H NMR δ 1.27 (t, 9H, J = 7.3 Hz), 3.89 (q, 6H, J = 7.3 Hz), 6.18 (d, 1H, J = 19.5 Hz), 7.13−7.44 (m, 6H); ^{13}C NMR δ 18.2, 58.5, 117.6, 126.7, 128.5, 128.7, 137.6, 149.1.

1-(Triethoxysilyl)-2-phenylethane (3g):[22] ^{1}H NMR δ 0.97−1.03 (m, 2H), 1.23 (t, 9H, J = 6.9 Hz), 2.71−2.77 (m, 2H), 3.82 (q, 6H, J = 6.9 Hz), 7.15−7.49 (m, 5H); ^{13}C NMR δ 12.5, 18.2, 28.8, 58.3, 125.6, 127.7, 128.2, 144.5.

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(21) Yamamoto, K.; Hayashi, T.; Uramoto, Y.; Ito, R.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 331.
(22) Lewis, L. *J. Am. Chem. Soc.* **1990**, *112*, 5998.