RhCl(PPh$_3$)$_3$ catalyzed hydrosilylation of styrene and phenylacetylene with phenylsilanes

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Abstract

Reaction of styrene with Ph$_2$SiH$_2$ catalyzed by RhCl(PPh$_3$)$_3$ (<0.3 mol%) proceeds smoothly in THF to give Ph$_2$SiH(CH$_2$CH$_2$Ph) in 77–89% yields although the reaction is accompanied by formation of Ph$_2$SiH(CH=CHPh), ethylbenzene, and Ph$_3$SiH in small amounts. Similar reaction in toluene also gives a mixture of Ph$_2$SiH(CH$_2$CH$_2$Ph), Ph$_2$SiH(CH=CHPh), ethylbenzene, and Ph$_3$SiH with lower yield of the hydrosilylation product than the reaction in THF. Reaction of styrene with Ph$_2$SiD$_2$ catalyzed by RhCl(PPh$_3$)$_3$ in toluene gives a mixture of these products which are partly deuterated on the non-aromatic hydrogens. The ^{1}H NMR spectrum of the products indicates complete deuterium scrambling on the hydrogen atoms of styrene and the phenylsilanes prior to or during the reaction. Further reaction of Ph$_2$SiH(CH$_2$CH$_2$Ph) with HSPh catalyzed by RhCl(PPh$_3$)$_3$ gives Ph$_2$Si(SPh)(CH$_2$CH$_2$Ph). Hydrosilylation of styrene with PhSiH$_3$ catalyzed by RhCl(PPh$_3$)$_3$ is much slower than the reaction with Ph$_2$SiH$_2$. Hydrosilylation of phenylacetylene with PhSiH$_3$ catalyzed by 0.1 mol% of RhCl(PPh$_3$)$_3$ gives PhSiH$_2$(CH=CHPh) in 67% as the sole reaction product. Similar reaction of 1-octyne gives PhSiH$_2$[CH=CH(CH$_2$)$_5$Me]. These hydrosilylation products are converted into thiolato substituted organosilane through RhCl(PPh$_3$)$_3$ catalyzed dehydrogenative condensation with HSAr (Ar = C$_6$H$_5$, C$_6$H$_4$-p-Me, C$_6$H$_4$-o-Me).

Keywords: Alkene; Alkyne; Arylsilanes; Hydrosilylation; Rhodium; Thiol

1. Introduction

Transition metal complex catalyzed hydrosilylation of alkenes, alkynes as well as dienes provides a useful tool for synthesis of organosilicon compounds [1]. Since discovery of hydrosilylation of C=C double bond catalyzed by Rh complex [2], reactions of alkenes with alkyl-and arylsilanes to lead to Si–C bond formation have been examined by using several Rh complexes as the catalysts [3–11]. RhCl(PPh$_3$)$_3$ catalyzed hydrosilylation of 1-alkene or styrene proceeds smoothly under mild conditions, but the reaction is often accompanied by hydrogenation and/or dehydrogenative silylation of olefins as shown in Scheme SCHEME [4–6,8,11].

Most previous studies on RhCl(PPh$_3$)$_3$ catalyzed hydrosilylation of alkenes have used trialkylsilanes as the substrate. The reaction of styrene with Et$_3$SiH at 65°C in toluene was reported to give a mixture of hydrosilylation products, Et$_3$SiCH$_2$CH$_2$Ph (23%) and Et$_3$SiCH(Me)Ph (10%), as well as ethylbenzene in 40% yield [8]. Similar hydrosilylation with diorganosilanes would give different results since reactivity and selectivity of similar hydrosilyla-
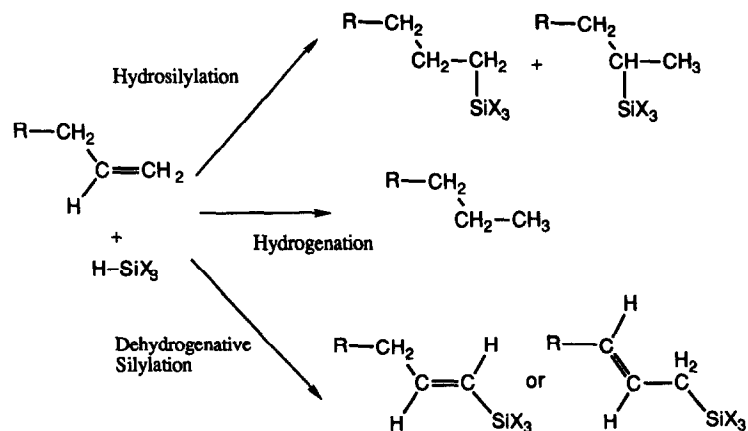
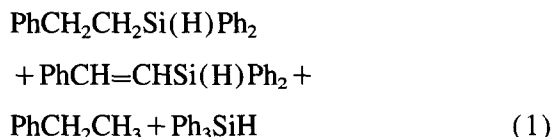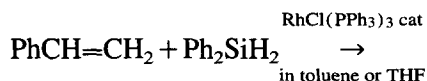Scheme 1. RhCl(PPh₃)₃ catalyzed reactions of 1-alkene with hydrosilane.

tion of alkenes catalyzed by Pt complexes varies depending on the kind of organosilane used. However, there have been few reports on detailed results of the reactions of alkenes with diorganosilanes catalyzed by RhCl(PPh₃)₃. In this paper we report that the reaction using Ph₂SiH₂ at room temperature in THF gives the hydrosilylation product through anti-Markovnikov addition in much higher yield and selectivity than the already reported reaction using trialkylsilane and that the reaction of phenylacetylene with PhSiH₃ gives *trans*-PhSiH₂(CH=CHPh) exclusively. Results of deuterium labeling experiments for the former reaction are also described.

2. Results and discussion

2.1. RhCl(PPh₃)₃ catalyzed hydrosilylation of styrene with Ph₂SiH₂

RhCl(PPh₃)₃ catalyzed hydrosilylation of styrene with Ph₂SiH₂ in THF proceeds smoothly at room temperature to give Ph₂SiH(CH₂CH₂Ph) as the major product. Table 1 shows results of the hydrosilylation under various conditions. The product Ph₂SiH(CH₂CH₂Ph) is isolated in 77–89% when the reaction is carried out in THF in high substrate to catalyst ratios (> 350) (runs 1–3). Another possible hydrosilylation product, Ph₂SiH[CH(CH₃)Ph], is not formed at all. Formation of several minor products,

Ph₂SiH(CH=CHPh), Ph₃SiH and ethylbenzene, is also observed. The reaction with lower substrate to catalyst ratio (100) gives the by-products in higher yields (run 4) although the reaction is completed in a shorter period.

$$PhCH=CH_2 + Ph_2SiH_2 \xrightarrow[\text{in toluene or THF}]{\text{RhCl(PPh}_3)_3 \text{ cat}}$$

$$PhCH_2CH_2Si(H)Ph_2$$

$$+ PhCH=CHSi(H)Ph_2 +$$

$$PhCH_2CH_3 + Ph_3SiH \qquad (1)$$

Reaction of styrene with Ph₂SiH₂ in toluene gives a mixture of the above compounds although the yield of the hydrosilylation product is lower than that in THF (runs 5 and 6).

Fig. 1 shows the ¹H NMR spectrum of the mixture of the reaction carried out in toluene-d_8 in a sealed NMR tube. Peaks due to the SiH and CH₂ hydrogens of Ph₂SiH(CH₂CH₂Ph) are observed at 5.02, 2.70 and 1.40 ppm with splitting due to HH coupling. Peaks due to Ph₂SiH(CH=CHPh) through dehydrogenative silylation is not observed although the spectrum at the initial stage of the reaction shows the presence of the compound. The unsaturated product seems to undergo hydrogenation to give the saturated silane under the conditions. The presence of Ph₂SiH(CH=CHPh) in the products of reactions (run 5 and 6) in tblr1 in spite of the absence of the diphenyl(styryl)silane in the reaction of Fig. 1 is attributed to difference in the reaction

conditions. The former reaction under Ar stream causes elimination of H_2, while effective hydrogenation of $Ph_2SiH(CH=CHPh)$ by H_2 evolved during the reaction is observed in the latter reaction carried out in a sealed NMR tube.

The singlet peak at 5.62 ppm in Fig. 1 is assigned to Ph_3SiH formed during the reaction. Previously $RhCl(PPh_3)_3$ has been reported to catalyze conversion of Ph_2SiH_2 at 80°C or at room temperature into a mixture of organosilicon compounds containing $Ph_2SiHSiHPh_2$ and Ph_3SiH [12]. Hydrosilylation of methyl methacrylate catalyzed by $RhCl(PPh_3)_3$ at room temperature also gave the disilane as a by-product although the reaction details are not shown in the report [8]. Formation of disilane catalyzed by Rh complexes was reported in the reaction of Et_2SiH_2 in the presence of $RhCl(PPh_3)_3$ at room temperature [13]. However, the ^1H NMR spectrum of the present reaction mixture shows the absence of $Ph_2SiHSiHPh_2$ that should show the SiH hydrogen peak at 5.16 ppm [6]. Ph_3SiH in the reaction mixture seems to be formed through disproportionation of Ph_2SiH_2 through phenyl group migration catalyzed by the Rh complex although the counterpart $PhSiH_3$ is not observed in the reaction mixture. Rapid disappearance of $PhSiH_3$ through hydrosilylation of the olefin does not account for the absence of $PhSiH_3$ in the final reaction mixture since the reaction of styrene with $PhSiH_3$ cata-
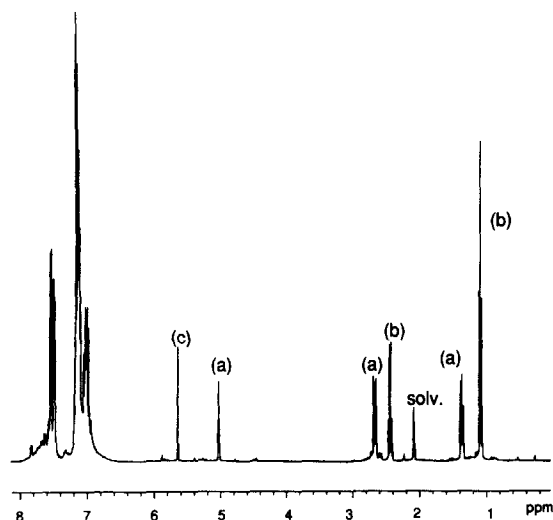

Fig. 1. The ^1H NMR spectrum (400 MHz, toluene-d_8) of the reaction mixture of styrene with Ph_2SiH_2 in the presence of $RhCl(PPh_3)_3$ catalyst (1 mol%) after 24 h at 25°C. Peaks with (a), (b), and (c) are due to (2-phenylethyl)diphenylsilane, ethylbenzene, and triphenylsilane, respectively.

lyzed by $RhCl(PPh_3)_3$ is much slower than that with Ph_2SiH_2 (vide infra).

Fig. 2 shows the change in the amounts of starting materials and products in equimolar reaction of styrene and Ph_2SiH_2 catalyzed by $RhCl(PPh_3)_3$ in toluene. Amounts of styrene and Ph_2SiH_2 decrease rapidly during the initial 100 min. After 100 min consumption of styrene as well as formation of $Ph_2SiH(CH_2CH_2Ph)$, $Ph_2SiH(CH=CHPh)$, and ethylbenzene become much slower than before. On keeping the reaction

Table 1
$RhCl(PPh_3)_3$ catalyzed hydrosilylation of styrene with Ph_2SiH_2 [a]

Run	Substrate (mmol)		Conditions		Product (mmol) [b]			
	$PhCH=CH_2$	Ph_2SiH_2	solvent	time (h)	$Ph_2SiH(CH_2CH_2Ph)$ [c]	$Ph_2SiH(CH=CHPh)$ [d]	$PhCH_2CH_3$ [d]	Ph_3SiH [d]
1	7.5	7.1	THF	24	5.9 (79) [83]	[e]	0.42 (6)	0.30 [4]
2	5.5	5.5	THF	20	4.9 (89) [89]	0.06 (1) [1]	0.36 (7)	0.19 [3]
3	3.5	3.5	THF	3.5	2.7 (77) [77]	0.06 (2) [2]	[e]	0.15 [4]
4	1.4	1.0	THF	0.5	0.55 (39) [55]	0.04 (4) [4]	0.26 (26)	0.13 [13]
5	1.0	1.0	toluene	2.0	0.39 (39) [39]	0.29 (29) [29]	0.28 (28)	0.21 [21]
6 [f]	1.0	1.0	toluene	3.5	0.47 (47) [47]	0.13 (13) [13]	[e]	0.15 [15]

[a] Reactions were carried out under Ar stream in the presence of $RhCl(PPh_3)_3$ (10 mg, 0.010) in the solvent (2 ml) at 25°C.
[b] Yields based on styrene and on Ph_2SiH_2 are shown in parenthesis and in brackets, respectively.
[c] Isolated yields.
[d] Yields by ^1H NMR. See Experimental, Section 4.2, for details.
[e] Formation was confirmed, but the yield was not determined.
[f] The reaction was carried out by addition of Ph_2SiH_2 to the solution containing styrene and the catalyst with stirring.
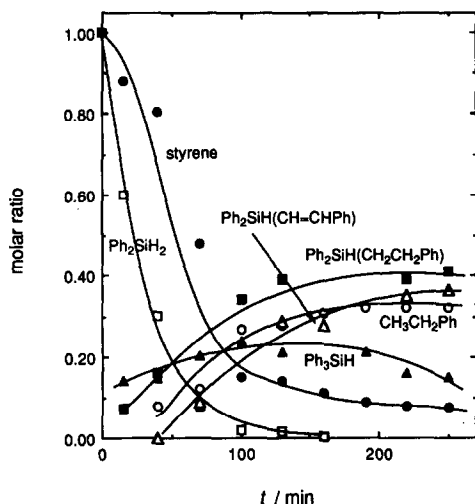
Fig. 2. Change of the amounts of starting materials and products during the RhCl(PPh₃)₃ catalyzed reaction of styrene with Ph_2SiH_2 in toluene-d_8. See Section 4.2 for the reaction conditions.

mixture for a further 24 h, partial hydrogenation of $Ph_2SiH(CH=CHPh)$ into $Ph_2SiH(CH_2CH_2Ph)$ is observed. All these observations suggest that Ph_2SiH_2 causes hydrosilylation, dehydrogenative silylation as well as hydrogenation of styrene rapidly in the initial period of the reaction and that formation of $Ph_2SiH(CH_2CH_2Ph)$ is partly attributed to gradual hydrogenation of initially formed $Ph_2SiH(CH=CHPh)$.

$RhCl(PPh_3)_3$ catalyzed hydrosilylation of 1-alkenes with trialkylsilane has been already reported to give alkane as a by-product from hydrogenation of the alkene. Hydrogen source is believed to be dihydrogen evolved through dehydrogenative silylation. On the other hand, Ph_2SiH_2 is able to provide hydrogen atoms to the alkene also through dehydrogenative condensation to give disilane or oligosilanes catalyzed by the Rh complex [12,14]. In order to explore hydrogen source of the hydrogenation in the present study several reactions were examined as shown below.

Products in the reaction in toluene-d_8 do not contain deuterium at the CH_2 and CH_3 position. Ethylbenzene formed from the reaction in the presence of excess D_2O in THF-d_8 is not deuterated although hydrosilylation product is not well characterized due to further reaction of Si–H bond

with D_2O under the conditions. The results indicate that hydrogen source in the hydrogenation is not the solvent nor H_2O in the mixture but hydrogens contained in the substrate molecules. Reaction of styrene with Ph_2SiD_2 catalyzed by $RhCl(PPh_3)_3$ in toluene-d_8 also gives a mixture of (2-phenylethyl)diphenylsilane, ethylbenzene and triphenylsilane. Fig. 3 shows the ¹H NMR spectrum of the reaction mixture showing the peaks due to SiH, PhCH₂ (or PhCHD), and SiCH₂ (or SiCHD) hydrogens of (2-phenylethyl)diphenylsilane in a 43:100:96 peak area ratio which agrees with the ratio of hydrogens in the molecule (1:2:2). The above peaks except for that of SiH are with complicated splitting due to both HH and HD coupling. Peak area ratio between CH_2 (or CHD) and CH_3 (CH_2D or CHD_2) hydrogens in ethylbenzene (71:100) is also similar to the ratio of the hydrogen atoms in the molecule (2:3). The peak due to ¹H of Ph_3SiH is observed at 5.62 ppm. The ratio between peak areas of phenyl hydrogens and total peak areas of the SiH, CH_2 (or CHD), and CH_3 (CH_2D or CHD_2) hydrogens of the products agrees with that calculated from the amount of the starting materials. All the results indicate that non-aromatic hydro-
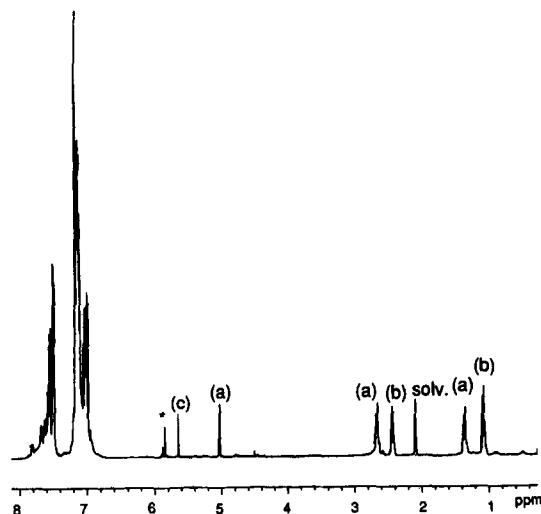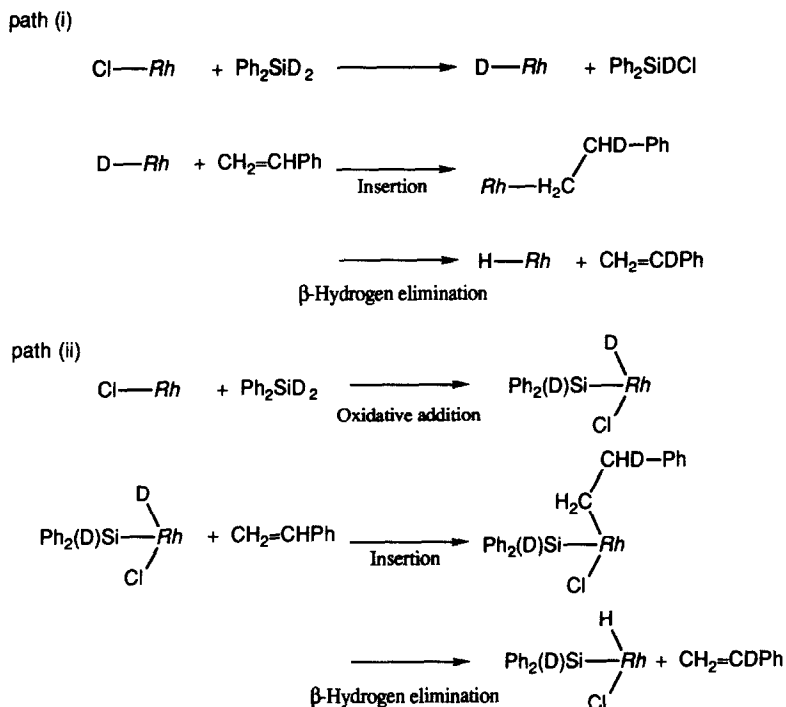

Fig. 3. The ¹H NMR spectrum (400 MHz, toluene-d_8) of the reaction mixture of styrene with Ph_2SiD_2 in the presence of $RhCl(PPh_3)_3$ catalyst (1 mol%) after 24 h at 25°C. Peaks with (a), (b), and (c) are due to (2-phenylethyl)diphenylsilane, ethylbenzene, and triphenylsilane, respectively. Peaks with asterisk are not assigned.

path (i)

$$Cl\!-\!Rh \;+\; Ph_2SiD_2 \;\longrightarrow\; D\!-\!Rh \;+\; Ph_2SiDCl$$

$$D\!-\!Rh \;+\; CH_2\!=\!CHPh \;\xrightarrow{\text{Insertion}}\; Rh\!-\!H_2C\diagup^{\displaystyle CHD\!-\!Ph}$$

$$\longrightarrow\; H\!-\!Rh \;+\; CH_2\!=\!CDPh$$
β-Hydrogen elimination

path (ii)

$$Cl\!-\!Rh \;+\; Ph_2SiD_2 \;\xrightarrow{\text{Oxidative addition}}\; Ph_2(D)Si\overset{\displaystyle D}{\underset{\displaystyle Cl}{\diagdown\,\diagup}}Rh$$

$$Ph_2(D)Si\overset{\displaystyle D}{\underset{\displaystyle Cl}{\diagdown\,\diagup}}Rh \;+\; CH_2\!=\!CHPh \;\xrightarrow{\text{Insertion}}\; Ph_2(D)Si\overset{\displaystyle H_2C\diagup^{CHD-Ph}}{\underset{\displaystyle Cl}{\diagdown\,\diagup}}Rh$$

$$\longrightarrow\; Ph_2(D)Si\overset{\displaystyle H}{\underset{\displaystyle Cl}{\diagdown\,\diagup}}Rh \;+\; CH_2\!=\!CDPh$$
β-Hydrogen elimination

Scheme 2. Plausible pathways for $RhCl(PPh_3)_3$ catalyzed deuterium scrambling ($Rh = Rh(PPh_3)_n$; only pathways via β-insertion are shown although α-insertion also occurs during the reaction).

gens of the substrates are scrambled rapidly prior to or during the reaction although the hydrogen source in the hydrogenation is not determined unambiguously.

Scheme SCHEME shows plausible pathways for the deuterium scrambling reaction. Path (i) involves initial formation of deuteriorhodium(I) intermediate that undergoes insertion of styrene into the Rh–D bond and ensuing β-hydrogen elimination.

Reactions of organosilane with chloro-iridium and -platinum complexes to give the corresponding hydride complexes have been already reported [14]. Reversible insertion of styrene into Rh–D bond of deuteriorhodium(III) intermediate followed by β-hydrogen elimination in path (ii) is also plausible. Deuteration of CH and CH_2 group of styrene in Scheme SCHEME prior to hydrosilylation or hydrogenation accounts for deuterium distribution in the hydrosilylation product. Deuterium labeling in both CH_2 and CH_3 positions of ethylbenzene is due to the deuteration of styrene as well as to reaction of styrene with D_2.

Previously $RhCl(PPh_3)_3$ catalyzed dehydrogenative condensation of Si–H group of organosilane with thiol was reported to give the corresponding thiolatosilane accompanied by H_2 evolution under mild conditions [15,16]. In order to examine reactivity of the SiH group of $Ph_2SiH(CH_2CH_2Ph)$, reaction with benzenethiol was examined. The reaction proceeds smoothly in the presence of $RhCl(PPh_3)_3$ catalyst to give $Ph_2Si(SPh)(CH_2CH_2Ph)$ in 91% yield.

$$Ph_2SiH(CH_2CH_2Ph)$$
$$+\,HSPh \;\xrightarrow{RhCl(PPh_3)_3\ cat}\; Ph_2Si(SPh)(CH_2CH_2Ph)$$

(2)
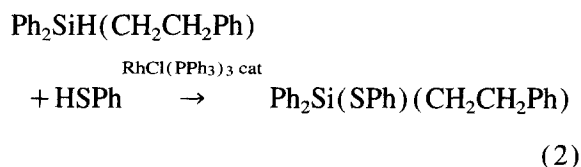
Direct reaction of Ph_2SiH_2, styrene and HSPh in a 1:1:1 molar ratio in the presence of $RhCl(PPh_3)_3$ (1 mol%) gives $Ph_2Si(SPh)(CH_2CH_2Ph)$ in 33% yield (by ^1H NMR peak area), while the reaction mixture contains unreacted styrene (30%), ethylbenzene (39%) and $Ph_2SiH(SPh)$ (67%) also. Similar reaction in a 1:1:2 molar ratio leads quantitative
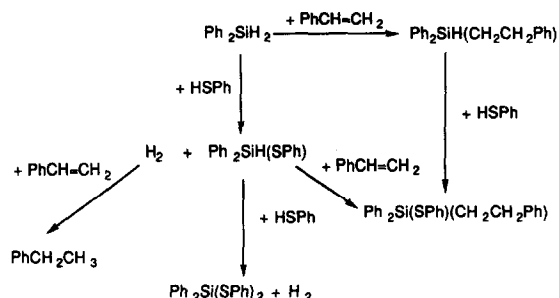
Scheme 3. RhCl(PPh$_3$)$_3$ catalyzed reaction of styrene with Ph$_2$SiH$_2$ in the presence of HSPh.

formation of ethylbenzene and Ph$_2$Si(SPh)$_2$. Ethylbenzene seems to be formed by reaction of styrene with H$_2$ evolved in the dehydrogenative condensation catalyzed by the Rh complex. These results suggest that dehydrogenative condensation of Ph$_2$SiH$_2$ with HSPh occurs more easily than the hydrosilylation of styrene with Ph$_2$SiH$_2$. Scheme SCHEME summarizes the reaction products of Ph$_2$SiH$_2$ and styrene in the presence of HSPh. Ph$_2$Si(SPh)(CH$_2$CH$_2$Ph) seems to be formed both through hydrosilylation of styrene with Ph$_2$SiH(SPh) and through condensation of Ph$_2$SiH(CH$_2$CH$_2$Ph) and HSPh.

2.2. RhCl(PPh$_3$)$_3$ catalyzed hydrosilylation of styrene and phenylacetylene with PhSiH$_3$

Hydrosilylation of styrene with PhSiH$_3$ proceeds much more slowly than the reaction with Ph$_2$SiH$_2$ and gives only negligible amounts of hydrosilylated products after 24 h at room temperature. However, reaction of phenylacetylene with PhSiH$_3$ in the presence of 0.1 mol% of the substrates proceeds smoothly at room temperature to cause exclusive formation of the hydrosilylation product PhSiH$_2$(CH=CHPh).

$$\text{PhC=CH} + \text{PhSiH}_3 \quad \xrightarrow{\text{RhCl(PPh}_3)_3 \text{ cat}}$$

$$\textit{trans-}\text{PhSiH}_2(\text{CH=CHPh}) \qquad (3)$$
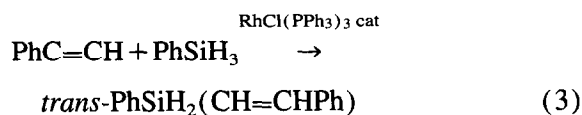
The ^{1}H NMR spectrum of the product shows peaks due to a vinylic hydrogen at 6.6 ppm whose large J(HH) value (19 Hz) agrees with the trans structure. The absence of the cis isomer in the reaction mixture suggests cis addition of Si–H

bond to C=C triple bond in the reaction. The high regio-and stereoselectivity of the present reaction is remarkable when compared with the hydrosilylation of phenylacetylene with trialkylsilanes catalyzed by Rh(acac)(C$_2$H$_4$)$_2$ giving mixtures of the regio and stereo isomers already reported [9].

Similar hydrosilylation of 1-octyne with PhSiH$_3$ also gives PhSiH$_2$[CH=CH(CH$_2$)$_5$CH$_3$] although isolation of the product from the reaction mixture was not feasible due to contamination with PhSiH$_3$ and Ph$_2$SiH$_2$ contained in the reaction mixture. The ^{1}H NMR spectrum of the reaction mixture indicates the absence of the isomers of the product such as cis-PhSiH$_2$[CH=CH(CH$_2$)$_5$CH$_3$], PhSiH$_2$[C(=CH$_2$)(CH$_2$)$_5$CH$_3$] as well as PhSiH$_2$[CH$_2$CH=CH(CH$_2$)$_4$CH$_3$]. Ojima and his co-workers have established cis addition of trialkylsilane to 1-hexyne catalyzed by Rh carbonyl complexes [17].

Reactions of PhSiH$_2$(CH=CHPh) with HSAr (Ar = C$_6$H$_5$, C$_6$H$_4$-p-Me, C$_6$H$_4$-o-Me) in the presence of RhCl(PPh$_3$)$_3$ catalyst give thiolato group substituted products, PhSi(SAr)$_2$(CH$_2$CH$_2$Ph), in high yields.

$$\text{PhSiH}_2(\text{CH=CHPh}) + 2\text{HSAr} \quad \xrightarrow{\text{RhCl(PPh}_3)_3 \text{ cat}}$$

$$\text{PhSi(SAr)}_2(\text{CH}_2\text{CH}_2\text{Ph}) \qquad (4)$$
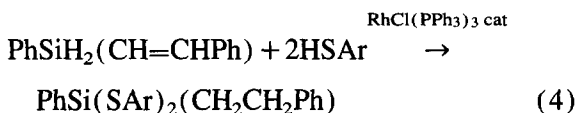
The C=C double bond of the substrates is reduced by H$_2$ evolved from the condensation of SiH and SH groups during the reactions.

3. Conclusion

RhCl(PPh$_3$)$_3$ catalyzed hydrosilylation of styrene with Ph$_2$SiH$_2$ in THF gives the product with higher selectivity than the already reported reactions using trialkylsilane as the substrate. Reaction of phenylacetylene with PhSiH$_3$ leads formation of PhSiH$_2$(CH=CHPh) with high regio-and stereoselectivity. These hydrosilylation products are converted into the thiolato group substituted

derivatives through condensation with HSAr in the presence of $RhCl(PPh_3)_3$ catalyst.

4. Experimental

4.1. General procedure, materials, and measurement

All the manipulations of the complexes were carried out under nitrogen or argon atmosphere using standard Schlenk technique. The solvents were dried in a usual manner, distilled, and stored under argon. Ph_2SiH_2, $PhSiH_3$, styrene, phenylacetylene, 1-octyne, and thiols were purchased from Tokyo Kasei Co. NMR spectra (^1H and ^{13}C) were recorded on JEOL EX-90 and EX-400 spectrometers. Elemental analyses were carried out by Yanagimoto Type MT-2 CHN autocorder. GC measurement was carried out on a Shimadzu GC-8A gas chromatograph equipped with a 2 m column packed with SE-30.

4.2. Hydrosilylation of styrene with Ph_2SiH_2

To a THF (2 ml) solution of $RhCl(PPh_3)_3$ (10 mg, 0.011 mmol) was added a mixture of Ph_2SiH_2 (1.3 g, 7.1 mmol) and styrene (0.78 g, 7.5 mmol) with stirring. The stirring was continued for 24 h at room temperature under Ar stream. A small portion (3 vol%) of the resulting red solution was analyzed by H NMR after removal of the solvent and dissolving the product in $CDCl_3$. Peaks due to $Ph_2SiH(CH_2CH_2Ph)$, $Ph_2SiH(CH=CHPh)$ (29%), ethylbenzene (28%), and Ph_3SiH (21%) were observed. The NMR yields of the latter three compounds were determined by relative peak area to dioxane as the internal standard. The remaining solution was passed through a short Florisil column to remove the catalyst. The liquid product thus obtained was further purified by column chromatography over neutral alumina to give $Ph_2SiH(CH_2CH_2Ph)$ (1.7 g, 79%). Anal. calcd. for $C_{20}H_{20}Si$: C, 83.3; H, 7.0. Found: C, 83.3; H, 6.7. ^1H NMR ($CDCl_3$) $\delta = 7.8$–7.0 (m, 15H, C_6H_5), 4.9 (t, $J = 5$ Hz, 1H, SiH), 2.8 (m, 2H,

CH_2), 1.4 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta = 144.2$, 135.1, 134.1, 129.6, 128.3, 127.8, 125.7, 30.4, 14.0.

The hydrosilylation in an NMR tube was carried out as follows. A 5 mm ϕ NMR tube containing $RhCl(PPh_3)_3$ (1 mg, 0.001 mmol) was sealed with a rubber septum under Ar atmosphere. Toluene-d_8 (ca. 0.4 ml), Ph_2SiH_2 (18 mg, 0.098 mmol) and styrene (10 mg, 0.096 mmol) were injected in this order with a syringe through septum. After shaking to dissolve the catalyst the reaction mixture was kept at room temperature. Amounts of the products and unreacted substrates were determined periodically by peak area ratio of the compounds relative to that of the solvent.

4.3. Reaction of $Ph_2SiH(CH_2CH_2Ph)$ with PhSH by $RhCl(PPh_3)_3$ catalyst

To a toluene (2 ml) solution of $Ph_2SiH(CH_2CH_2Ph)$ (290 mg, 1.0 mmol) and PhSH (110 mg, 1.0 mmol) was added $RhCl(PPh_3)_3$ (14 mg, 0.015 mmol). After vigorous hydrogen evolution ceased the reaction mixture was stirred for 4 h at room temperature. The reaction mixture was diluted with hexane (50 ml) and passed through a short Florisil column to remove the catalyst. Evaporation of the solvent under vacuum gives $Ph_2Si(SPh)(CH_2CH_2Ph)$ as a viscous liquid (360 mg, 91%). Anal. calcd. for $C_{26}H_{24}SSi$: C, 78.7; H, 6.1. Found: C, 78.7; H, 6.4. ^1H NMR ($CDCl_3$) $\delta = 7.9$–6.7 (m, 20H, C_6H_5), 2.8 (m, 2H, CH_2), 1.5 (m, 2H, CH_2).

4.4. Hydrosilylation of phenylacetylene with $PhSiH_3$

To a mixture of $PhSiH_3$ (110 mg, 10 mmol) and phenylacetylene (1.2 g, 12 mmol) was added $RhCl(PPh_3)_3$ (11 mg, 0.012 mmol) with stirring. After stirring the reaction mixture for 18 h at room temperature the product was diluted with hexane (100 ml), and the catalyst was removed by passing a short Florisil column. The following distillation of the product gave $trans$-$PhSiH_2(CH=CHPh)$ (1.4 g, 67%). Anal.

calcd. for $C_{14}H_{14}Si$: C, 80.0; H, 6.7. Found: C, 80.8; H, 6.7. ^1H NMR ($CDCl_3$) $\delta = 7.8–7.0$ (m, 11H, C_6H_5 and CH=), 6.6 (dt, 1H, $J = 19$ Hz, 3 Hz, CH=), 4.8 (d, 2H, $J = 3$ Hz, SiH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta = 149.9$, 135.8, 130.1, 129.1, 128.8, 128.4, 127.1, 126.9, 119.5.

Reaction of 1-octyne with $PhSiH_3$ was carried out analogously. The product after work-up similar to above reaction contains a mixture of $PhSiH_2[CH=CH(CH_2)_5CH_3]$ and small amounts of $PhSiH_3$ and Ph_2SiH_2 as revealed by the ^1H NMR spectra. ^1H NMR ($CDCl_3$) $\delta = 7.7–7.0$ (m, 5H, C_6H_5), 6.3 (dt, 1H, $J = 18$, 6 Hz, CH=), 5.7 (dtt, 1H, $J = 18$, 3, 1 Hz, Si–CH=), 4.5 (d, 2H, $J = 3$ Hz, SiH), 2.2 (m, 2H, CH_2), 1.5–0.8 (m, 11H, CH_2 and CH_3).

4.5. $RhCl(PPh_3)_3$ catalyzed reaction of $PhSiH_2(CH=CHPh)$ with aromatic thiol

To a well stirred toluene (2 ml) solution of $PhSiH_2(CH=CHPh)$ (210 mg, 1.0 mmol) and PhSH (220 mg, 2.0 mmol) was added $RhCl(PPh_3)_3$ (10 mg, 0.011 mmol) at room temperature. After stirring at room temperature for 24 h the resulting red solution was eluted through Florisil (2 g) short column to remove the catalyst. Evaporation of the solvent from the eluant gave $PhSi(SPh)_2(CH_2CH_2Ph)$ as colorless liquid (400 mg, 93%). Anal. calcd. for $C_{26}H_{24}S_2Si$: C, 72.8; H, 5.6. Found: C, 73.8; H, 6.0. ^1H NMR ($CDCl_3$) $\delta = 7.8–6.8$ (m, 20H, C_6H_5), 2.5 (m, 2H, CH_2), 1.2 (m, 2H, CH_2).

Reactions with other thiols were carried out analogously. $PhSi(SC_6H_4-p-Me)_2(CH_2CH_2Ph)$ was obtained in 88% yield. Anal. calcd. for $C_{28}H_{28}S_2Si$: C, 73.7; H, 6.1. Found: C, 72.9; H, 6.0. ^1H NMR ($CDCl_3$) $\delta = 7.8–6.8$ (m, 18H, aromatic), 2.5 (m, 2H, CH_2), 2.1 (s, 6H, CH_3), 1.2 (m, 2H, CH_2). $PhSi(SC_6H_4-o-Me)_2(CH_2CH_2Ph)$ was obtained in 93% yield. Anal. calcd. for $C_{28}H_{28}S_2Si$: C, 73.7; H, 6.1. Found: C, 73.4; H, 6.0. ^1H NMR ($CDCl_3$) $\delta = 7.7–6.9$ (m, 18H, aromatic), 2.5 (m, 2H, CH_2), 2.3(s, 6H, CH_3), 1.4 (m, 2H, CH_2).

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