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Structure and Properties of Halogeno(hydrido)(triorganosilyl)rhodium(III) Complexes, $RhX(H)(SiR^1{}_nR^2{}_{3-n})(PPh_3)_2$ (X = Cl, I; $R^1 = OSiMe_3$, OEt, R^2 = Me). Influence of the Alkoxy Groups and Halo Ligand on Stability and Reactivity of the Complexes

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Silylrhodium(III) complexes $RhX(H)(SiR^1{}_nR^2{}_{3-n})(PPh_3)_2$ (**1**: X = I, $R^1 = OSiMe_3$, R^2 = Me, $n = 1$; **2**: X = I, R^1 = OEt, $n = 3$; **3**: X = I, R^1 = OEt, R^2 = Me, $n = 2$; **4**: X = I, R^1 = OEt, R^2 = Me, $n = 1$; **5**: X = Cl, $R^1 = OSiMe_3$, R^2 = Me, $n = 1$; **6**: X = Cl, R^1 = OEt, $n = 3$; **7**: X = Cl, R^1 = OEt, R^2 = Me, $n = 2$; **8**: X = Cl, R^1 = OEt, R^2 = Me, $n = 1$) were prepared by oxidative addition of $HSiR^1{}_nR^2{}_{3-n}$ to $RhX(PPh_3)_3$ and characterized by means of NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{29}Si\{^1H\}$) and IR spectroscopy as well as elemental analyses. X-ray crystallography of **1**, **2**, and **6** showed a distorted square-pyramidal coordination around the Rh center that is bonded to the silyl ligand at the apical position and to halo and hydrido ligands in trans positions in the basal plane. The Rh−Si bonds in **2** and **6** are the shortest among Rh−Si bonds of the silylrhodium complexes reported to date. $^{29}Si\{^1H\}$ NMR spectra of **1**−**8** show that the *J*(RhSi) value increases with an increase in the number of alkoxy substituents on the Si atom. Complex **2** reacted with $HSiMe_2(OSiMe_3)$, $HSi(OEt)_2Me$, and $HSi(OEt)Me_2$, respectively, to cause exchange of the silyl group between the Rh complex and the organosilane, forming an equilibrium mixture. Complexes **5**−**8** undergo thermally induced coupling of their chloro and triorganosilyl ligands at 60 °C to liberate the respective chloro(triorgano)silane. The reaction obeys first-order kinetics in the Rh complex with the observed rate constants in the order **5** $\cong$ **8** > **7** > **6**. The OEt groups at the Si retard the coupling of chloro and triorganosilyl ligands significantly. Formation of $ISiMe_2(OEt)_2$ from **4** takes place at a slightly slower rate than the reaction of **6**, while complexes **2** and **3** do not undergo coupling of their iodo and silyl ligands at 60 °C.

Introduction

The structure and chemical properties of silylrhodium complexes containing phosphine or cyclopentadienyl as ancillary ligands[1−15] have attracted attention during the past decades probably owing to their relationship to the mechanisms of Rh complex-catalyzed synthetic organic reactions such as hydrosilylation of alkene and carbonyl compounds and silylformylation of alkenes and alkynes.[16−18] Oxidative addition of di- or triorganosilanes to 16- or 14-electron Rh(I) complexes provides a convenient route to silylrhodium(III) complexes. $RhCl(PPh_3)_3$

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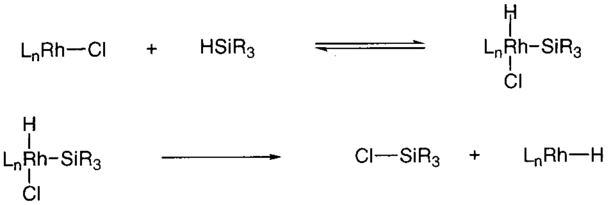
Scheme 1

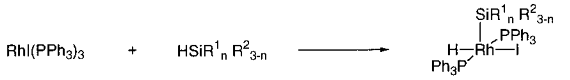


reacts with $HSiCl_3$ to give stable $RhCl(H)(SiCl_3)(PPh_3)_2$.[4] The reactions of $HSiR_3$ with chloroiridium(I) and dichloroplatinum(II) complexes containing PPh_3 ligands, however, produce $ClSiR_3$ via initial oxidative addition of $HSiR_3$ to give the Ir(III) or Pt(IV) intermediate followed by coupling of the chloro and silyl ligands.[19] Recently, we reported the oxidative addition of di- or triorganosilanes with $RhCl\{P(i\text{-}Pr)_3\}_2$ and $[Rh(PMe_3)_4]Cl$ to produce the rhodium(III) complexes with silyl, hydrido, and chloro ligands.[20,21] These complexes undergo coupling of their chloro and silyl ligands, giving chlorosilanes and hydridorhodium species as depicted in Scheme 1. Oxidative addition of $HSiR_3$ to Rh(I) occurs reversibly, whereas reductive elimination of $ClSiR_3$ is irreversible.[20f]

To obtain further insights into such coupling of halo and silyl ligands, we prepared several chloro(silyl)rhodium(III) and iodo(silyl)rhodium complexes containing PPh_3 ligands. Comparison of the stability and reactivity of iodo(silyl)rhodium(III) complexes with those of chloro(silyl)rhodium complexes is of interest because iodorhodium complexes often exhibit unique catalytic activity for addition of organosilanes or their coupling reactions.[22,23] In this paper we report preparation of silylrhodium(III) complexes with an alkoxy group on Si and their chemical properties, which vary depending on the halo ligand and on the number of OR substituents at Si.

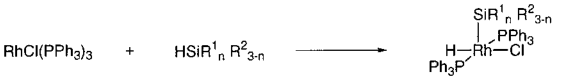
Results

$RhI(PPh_3)_3$ reacts with organosilanes, $HSiMe_2OSiMe_3$, $HSi(OEt)_3$, $HSi(OEt)_2Me$, and $HSi(OEt)Me_2$, at room temperature to produce silylrhodium(III) complexes, $RhI(H)(SiR^1{}_nR^2{}_{3-n})(PPh_3)_2$ (**1**: $R^1 = OSiMe_3$, $R^2 = Me$, $n = 1$; **2**: $R^1 = OEt$, $n = 3$; **3**: $R^1 = OEt$, $R^2 = Me$, $n = 2$; **4**: $R^1 = OEt$, $R^2 = Me$, $n = 1$), respectively (eq 1). Analogous oxidative addition reactions of alkoxy-substituted triorganosilanes to $RhCl(PPh_3)_3$ form the chloro(hydrido)silylrhodium(III) complexes, $RhCl(H)(SiR^1{}_nR^2{}_{3-n})(PPh_3)_2$ (**5**: $R^1 = OSiMe_3$, $R^2 = Me$, $n = 1$; **6**: $R^1 = OEt$, $n = 3$; **7**: $R^1 = OEt$, $R^2 = Me$, $n = 2$; **8**: $R^1 = OEt$, $R^2 = Me$, $n = 1$) (eq 2). Table 1 shows yields, analytical results, and IR data.



(1)

1: $R^1 = OSiMe_3$, $R^2 = Me$, n = 1
2: $R^1 = OEt$, n = 3
3: $R^1 = OEt$, $R^2 = Me$, n = 2
4: $R^1 = OEt$, $R^2 = Me$, n = 1



(2)

5: $R^1 = OSiMe_3$, $R^2 = Me$, n = 1
6: $R^1 = OEt$, n = 3
7: $R^1 = OEt$, $R^2 = Me$, n = 2
8: $R^1 = OEt$, $R^2 = Me$, n = 1

Figures 1−3 depict molecular structures of complexes **1**, **2**, and **6** as determined by X-ray crystallography. Table 2 summarizes selected bond distances and angles of the complexes. The molecules contain distorted square-pyramidal coordination with the silyl ligand at the apical site and the iodo or chloro ligand and the hydrido ligand in trans positions in the basal plane. We previously reported the reaction of triarylsilane with $RhCl\{P(i\text{-}Pr)_3\}_2$ to give $RhCl(H)(SiAr_3)\{P(i\text{-}Pr)_3\}_2$, which have square-pyramidal coordination analogous to **1**−**8**.[20c] The exclusive formation of the square-pyramidal complexes with PPh_3 and $P(i\text{-}Pr)_3$ as ancillary ligands among several possible structures is ascribed to a large trans effect of the silyl ligand, which may exclude structures with a ligand at the trans coordination site of the silyl ligand. $RhCl(H)(SiCl_3)(PPh_3)_2$[4] also contains the chloro, silyl, and hydrido ligands in meridional sites in this order in octahedral coordination; a C−H bond of a PPh_3 ligand coordinates weakly to the site trans to

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Table 1. Yields, Analytical Results, and IR Data of Complexes 1−8

complex	yield (%)[a]	anal. (%)[b] C	H	I or Cl	IR[c] ν(RhH)
RhI(H)(SiMe$_2$OSiMe$_3$) (PPh$_3$)$_2$ (**1**)	88	54.39 (54.55)	5.24 (5.14)	14.19 (14.06)	2124
RhI(H){Si(OEt)$_3$}(PPh$_3$)$_2$ (**2**)	86	55.15 (54.91)	5.04 (5.05)	13.82 (13.81)	2060
RhI(H){Si(OEt)$_2$Me}(PPh$_3$)$_2$ (**3**)	75	55.33 (55.42)	4.98 (4.99)	14.26 (14.28)	2076
RhI(H){Si(OEt)Me$_2$}(PPh$_3$)$_2$ (**4**)	76	56.01 (55.96)	5.02 (4.93)	14.60 (14.78)	2086
RhCl(H)(SiMe$_2$OSiMe$_3$) (PPh$_3$)$_2$ (**5**)[d]	86	62.52 (62.34)	5.52 (5.88)	4.03 (4.14)	2149
RhCl(H){Si(OEt)$_3$}(PPh$_3$)$_2$ (**6**)	79	60.94 (60.98)	5.82 (5.60)	3.94 (4.29)	2060
RhCl(H){Si(OEt)$_2$Me}(PPh$_3$)$_2$ (**7**)	97	61.62 (61.77)	5.59 (5.56)	4.23 (4.45)	2095
RhCl(H){Si(OEt)Me$_2$}(PPh$_3$)$_2$ (**8**)	89	63.97 (63.96)	5.48 (5.64)	4.56 (4.72)	2103

[a] Yields are before recrystallization, but their purity was confirmed by ^{1}H and ^{31}P{^{1}H} NMR spectra. [b] Calculated values are in parentheses. [c] cm^{-1} in KBr disks. [d] Obtained as **5**·0.5C$_7$H$_8$. The presence of solvated toluene was confirmed by ^{1}H NMR.

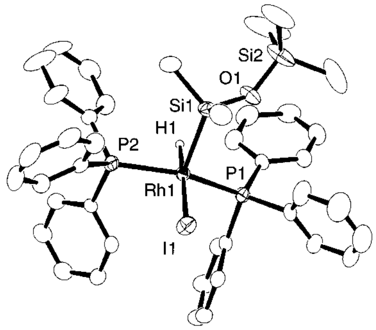

Figure 1. ORTEP drawing of RhI(H)(SiMe$_2$OSiMe$_3$)(PPh$_3$)$_2$ (**1**) at 50% ellipsoid level. One of the two crystallographically independent molecules is shown.

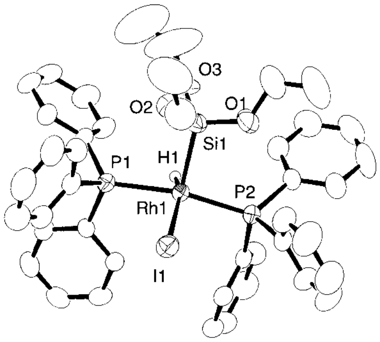

Figure 2. ORTEP drawing of RhI(H){Si(OEt)$_3$}(PPh$_3$)$_2$ (**2**) at 50% ellipsoid level.

the silyl ligand. The Rh−Si bond distances (2.291(2), 2.282(2) Å) of **1** are similar to the Rh−Si single bond of RhCl(H)(SiPh$_3$){P(*i*-Pr)$_3$}$_2$ (2.299(2) Å)[20c] and are shorter than those of octahedral RhH(SiPh$_3$)(SAr)(PMe$_3$)$_3$ (2.342(1) Å)[21c] due to the absence of a ligand in trans position to the silyl ligand in the pentacoordinated complexes. The Rh−Si distances in **2** (2.251(2) Å) and **6** (2.251(2) Å) are even shorter than that in **1** and than the Rh−Si single bond distances of the complexes already reported. Slight elongation of the Si−O bond of **1** (1.640(5) Å) compared with **2** (1.629(4), 1.634(4), 1.614(4) Å) was also noted.[24]

The IR peaks of the ν(RhH) vibration in the solid state are observed at 2149−2060 cm^{-1}, whose positions vary depending on substituents on the Si atom (Table 1). The wavenumbers of the peaks for the series of the iodo and chloro complexes decrease in the order **1** > **4** > **3** > **2** and **5** > **8** > **7** > **6**, respectively, indicating that the Rh−H bond becomes weaker on introduction of the alkoxy group on the Si center. This effect of the silyl ligand in cis position of the hydrido ligand on the IR data is much more significant than that of the Cl and I ligands, with a different trans influence, in trans positions of the hydrido ligand. The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR data of complexes **1**−**8** are listed in Tables 3 and 4. The NMR spectra of the complexes suggest that the structure in solution is the same as that in crystals of **1**, **2**, and, **6**. The ^{1}H NMR spectra of **1**−**4** show a characteristic Rh−H signal at δ −10.89 to −11.30 as a doublet of triplets with coupling constants of 25−26 Hz (J(RhH)) and 13−14 Hz (J(PH)). The hydrido signals of the chloro complexes **5**−**8** are observed at higher magnetic field (δ −13.98 to −14.09) with similar coupling constants. The ^{13}C{^{1}H} NMR signal of the ipso carbon of PPh$_3$ ligands of the complexes appears as an apparent triplet due to virtual coupling. These data indicate that the two PPh$_3$ ligands are in cis position to the hydrido ligand and are situated mutually in trans positions.

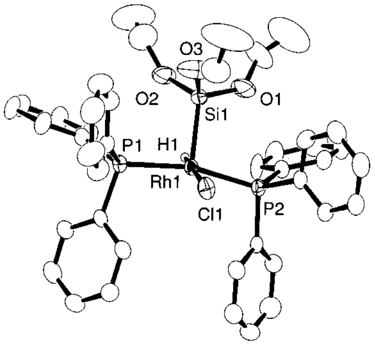

Figure 3. ORTEP drawing of RhCl(H){Si(OEt)$_3$}(PPh$_3$)$_2$ (**6**) at 50% ellipsoid level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1, 2, and 6

	1[a]		**2**	**6**
Rh−X[b]	2.724(1)	2.731(1)	2.7011(8)	2.401(2)
Rh−P1	2.320(2)	2.303(2)	2.324(2)	2.319(2)
Rh−P2	2.298(2)	2.297(2)	2.313(2)	2.319(2)
Rh−Si	2.291(2)	2.282(2)	2.251(2)	2.251(2)
X−Rh−P1[b]	95.04(6)	92.47(6)	90.54(4)	90.10(7)
X−Rh−P2[b]	99.08(6)	95.75(6)	94.64(4)	89.81(7)
P1−Rh−P2	152.82(8)	155.99(7)	162.11(6)	166.02(7)
Si−Rh−X[b]	106.27(7)	109.17(7)	114.81(5)	115.35(9)
Si−Rh−P1	101.17(9)	102.46(8)	96.78(6)	95.90(8)
Si−Rh−P2	97.00(9)	96.07(8)	96.54(6)	96.77(8)

[a] Data of two crystallographically independent molecules are shown. [b] X = I for **1** and **2**; X = Cl for **6**.

Table 5 summarizes the ^{29}Si{^{1}H} NMR data of **1**−**8** at −50 °C. The complexes give a doublet of triplets due to coupling with a Rh and two P nuclei. Complexes **1**, **4**, **5**, and **8** with a monoalkoxysilyl ligand show a J(RhSi) of 29 Hz, while other complexes exhibit larger coupling constants, 37 Hz for **3** and **7** and 49 Hz for **2** and **6**, respectively. This increase of J(RhSi) with the increase

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(24) The typical Si−O bond distance of siloxanes is 1.60 Å. See: Lickiss, P. D.; Litster, S. A.; Redhouse, A. D.; Wisener, C. J. *J. Chem. Soc., Chem. Commun.* **1991**, 173.

Table 3. ^{1}H NMR Data for Complexes 1−8[a]

	Rh−H	Si−Me	Si−OCH$_2$C*H*$_3$	Si−OC*H*$_2$CH$_3$	Ph
1	−11.27 (dt, 1H, J(RhH) = 25 Hz, J(PH) = 13 Hz)	−0.18 (s, 9H) 0.47 (s, 6H)			7.02−7.08 (m, 18H) 7.94−8.01 (m, 12H)
2	−10.89 (dt, 1H, J(RhH) = 26 Hz, J(PH) = 13 Hz)		0.91 (t, 9H, J = 7 Hz)	3.62 (q, 6H, J = 7 Hz)	7.00−7.15 (m, 18H) 7.95−8.02 (m, 12H)
3	−11.30 (dt, 1H, J(RhH) = 26 Hz, J(PH) = 14 Hz)	0.41 (s, 3H)	0.81 (t, 6H, J = 7 Hz)	3.36−3.57 (m, 4H)	7.00−7.15 (m, 18H) 7.95−8.02 (m, 12H)
4	−11.07 (dt, 1H, J(RhH) = 26 Hz, J(PH) = 14 Hz)	0.39 (s, 6H)	0.70 (t, 3H, J = 7 Hz)	3.20 (q, 2H, J = 7 Hz)	6.99−7.15 (m, 18H) 7.95−8.02 (m, 12H)
5	−14.09 (dt, 1H, J(RhH) = 24 Hz, J(PH) = 14 Hz)	−0.17 (s, 9H) 0.47 (s, 6H)			7.00−7.10 (m, 18H) 7.96−8.01 (m, 12H)
6	−13.98 (dt, 1H, J(Rh−H) = 24 Hz, J(PH) = 14 Hz)		0.90 (t, 9H, J = 7 Hz)	3.61 (q, 6H, J = 7 Hz)	7.04−7.07 (m, 18H) 7.95−8.02 (m, 12H)
7	−14.06 (dt, 1H, J(RhH) = 24 Hz, J(P−H) = 15 Hz)	0.42 (s, 3H)	0.83 (t, 6H, J = 7 Hz)	3.38−3.56 (m, 4H)	7.04−7.06 (m, 18H) 7.96−8.02 (m, 12H)
8	−14.06 (dt, 1H, J(RhH) = 24 Hz, J(PH) = 14 Hz)	0.38 (s, 6H)	0.72 (t, 3H, J = 7 Hz)	3.24 (q, 2H, J = 7 Hz)	7.02−7.07 (m, 18H) 7.96−8.03 (m, 12H)

[a] 300 MHz at 25 °C in benzene-d_6.

Table 4. ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR Data of Complexes 1−8

	^{13}C{^{1}H} NMR[a]							^{31}P{^{1}H} NMR[b]
	Si−Me	*C*H$_3$	*C*H$_2$	ortho[c]	meta[c]	para	ipso[d]	
1	1.84, 13.53[e]			128.43 (4.6)	135.20 (7.3)	130.39	133.41 (21.9)	43.5 (126.8)
2		17.74	59.12	128.20 (5.5)	135.22 (5.5)	130.21	133.39 (21.9)	43.1 (120.2)
3	5.19	17.81	58.79	128.23 (5.5)	135.09 (7.3)	130.23	133.74 (21.9)	42.4 (125.8)
4	9.71	17.81	58.90	128.36 (5.5)	135.15 (7.3)	130.34	133.66 (21.9)	42.3 (124.7)
5	1.86, 12.06[e]			128.54 (5.9)	135.15 (5.8)	130.45	133.16 (22.4)	42.2 (128.7)
6		17.96	58.90	128.53 (5.5)	135.38 (5.5)	130.52	133.28 (21.9)	41.5 (122.5)
7	4.39	17.70	58.65	128.34 (5.5)	135.07 (5.5)	130.32	133.39 (21.9)	40.6 (125.6)
8	8.08	17.54	58.48	128.16 (3.7)	134.80 (7.3)	130.10	132.99 (21.9)	40.0 (127.9)

[a] 100 MHz at 25 °C in benzene-d_6. [b] 121 MHz at 25 °C in benzene-d_6. Coupling constants, J(RhP) (Hz), are given in parentheses. [c] Observed splittings of the signals (Hz) are given in parentheses. [d] Apparent triplet due to virtual coupling. Observed splittings of the signals (Hz) are given in parentheses. [e] OSiMe$_3$ carbons.

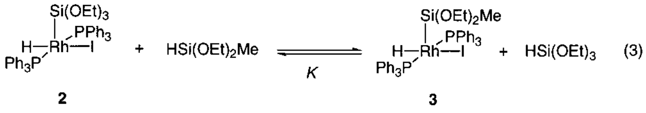
Table 5. ^{29}Si{^{1}H} NMR Data of Complexes 1−8[a]

	chemical shift (ppm)[b]			coupling constant (Hz)	
complex	$\delta_{\mathrm{complex}}$	$\delta_{\mathrm{HSiR^1_nR^2_{3-n}}}$	$\Delta\delta$[c]	^1J(RhSi)	^2J(PSi)
1[d]	44.42	−6.20	50.62	29.4	7.4
2	−39.78	−58.03	18.25	49.2	9.2
3	13.45	−16.02	29.47	36.8	7.4
4	54.14	4.79	49.35	29.4	7.4
5[d]	42.73	−6.20	48.93	29.4	7.4
6	−34.01	−58.03	24.02	49.6	9.2
7	15.44	−16.02	31.46	36.8	7.4
8	52.98	4.79	48.19	29.4	7.4

[a] 79.3 MHz at −50 °C in CD$_2$Cl$_2$. [b] Relative to SiMe$_4$. cf. δ −16.3 for HSiMe$_3$. [c] $\delta_{\mathrm{complex}} - \delta_{\mathrm{HSiR^1_nR^2_{3-n}}}$. [d] **1**, **5**, and HSiMe$_2$OSiMe$_3$ exhibit OSiMe$_3$ signals at δ 6.67, 6.62, and 10.30, respectively.

in the number of alkoxy substituents on Si is explained by more p-character of the Si−OR bond than that of the Si−C(sp^3) bond, which leaves more s-character of the Rh−Si bond (Bent's rule).[25] The difference of halo ligands of the complexes does not influence the magnitude of the coupling constants. The ^{29}Si{^{1}H} NMR peak positions vary depending on the number of alkoxy substituents on the Si center. The chemical shifts of Si(OEt)$_3$ complexes (δ −39.78 for **2** and δ −34.01 for **6**) are much lower than those of the other complexes. Dialkoxysilyl complexes show the signal at the positions (δ 13.45 for **3** and δ 15.44 for **7**) between the trialkoxysilyl complexes and the monoalkoxy complexes (δ 42.73−54.14 for **1**, **4**, **5**, and **8**). This order of δ values, Si(OEt)$_3$ < Si(OEt)$_2$Me < Si(OEt)Me$_2$, is observed also in the ^{29}Si{^{1}H} NMR spectra of the corresponding triorganosilanes, as listed in Table 5.[26] The magnitude of difference in δ values between the complex and the triorganosilane, $\Delta\delta$ ($\delta_{\mathrm{complex}} - \delta_{\mathrm{HSiR^1_nR^2_{3-n}}}$), increases significantly with a decrease in the number of alkoxy ligands at Si. The $\Delta\delta$ increases in the order **2** (18.25) < **3** (29.47) < **4** (49.35) ≅ **1** (50.62) in the iodo(silyl)rhodium(III) complexes and in the order **6** (24.02) < **7** (31.46) < **8** (48.19) ≅ **5** (48.93) in the chloro(silyl)rhodium(III) complexes. Complexes **1**, **4**, **5**, and **8**, having different alkoxy groups or different halo ligands, give quite similar $\Delta\ \delta$ values (48.19−50.62).

Hexacoordinated hydrido(silyl)rhodium complexes *mer*-RhCl(H)(SiHAr$_2$)(PMe$_3$)$_3$ were reported to react with added diarylsilanes to cause silyl group exchange via reductive elimination of diarylsilane and reoxidative addition of the other diarylsilane to the RhCl(PMe$_3$)$_3$.[20b] Analogous silyl group exchange reactions were conducted with the pentacoordinated iodo(silyl)rhodium(III) complexes **1**−**4**. Typically, complex **2** reacts with a mixture of an excess of HSiMe(OEt)$_2$ and HSi(OEt)$_3$ at 50 °C to give an equilibrium mixture of **2** and **3** (eq 3).



The reactions with HSiMe$_2$(OEt) and with HSiMe$_2$(OSiMe$_3$) lead to attainment of the equilibrium between **2** and **4** and between **1** and **2**, respectively. Equilibrium constants of the reactions were determined by measuring the relative ^{1}H NMR peak area ratios of the Si−H and Rh−H signals in the range 278−318 K (Table 6). Figure 4 shows van't Hoff plots of the reaction, which gives the thermodynamic parameters $\Delta H° = 1.37$ kJ mol^{-1} and $\Delta S° = 12$ J mol^{-1} K^{-1} for HSi(OEt)$_2$Me at

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(25) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

(26) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Chapter 8.

Table 6. Equilibrium Constants of Reaction of 2 with $HSiR_3$

	K^a		
temp (K)	$SiR_3 = SiMe_2OSiMe_3$	$Si(OEt)Me_2$	$Si(OEt)_2Me$
278	0.1011	0.346	2.27
288	0.1013	0.337	2.31
298	0.1015	0.331	2.36
308	0.1018	0.323	2.40
318	0.1020		2.44

[a] $K = [HSi(OEt)_3][RhI(H)(SiR_3)(PPh_3)_2][HSiR_3]^{-1}[\mathbf{2}]^{-1}$.

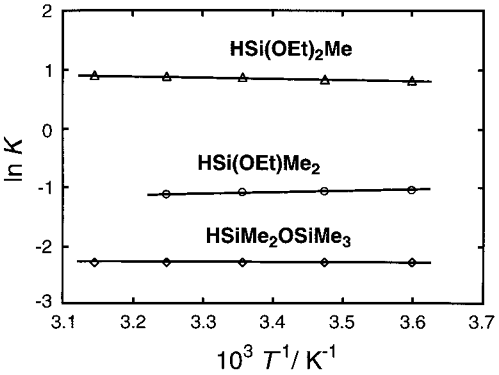
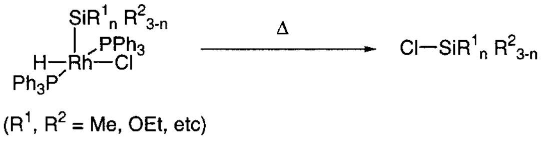


Figure 4. Van't Hoff plots of **2** with complexes **1**, **3**, and **4**. The equilibrium constants were obtained from NMR peak area ratios of the solutions of **2** with a mixture of excess $HSi(OEt)_3$ and triorganosilanes.

298 K. Measurement of analogous silyl exchange reactions of **2** with $HSiMe_2OSiMe_3$ and with $HSi(OEt)Me_2$ gave $\Delta H° = 0.17$ kJ mol^{-1} and $\Delta S° = -19$ J mol^{-1} K^{-1}, and $\Delta H° = -1.56$ kJ mol^{-1} and $\Delta S° = -14$ J mol^{-1} K^{-1}, respectively, at 298 K. The relative facility in formation of the complexes in these equilibrium silyl ligand exchanges is **3** > **2** > **4** ≅ **1**, which is not directly related to the number of alkoxy groups of the complexes.

The iodo(triorganosilyl)rhodium complexes **2** and **3** are stable above 60 °C in solution. Complex **4**, however, showed a decrease by 7% after being heated for 2 h at 60 °C. Thermal decomposition of chloro complex **6** at 60 °C occurs more rapidly (16% decrease in 2 h), and it forms 80% of $ClSi(OEt)_3$ after 24 h (eq 4). Complex **7** shows the first-order coupling of the chloro and triorganosilyl ligands, as plotted in Figure 5a. Complexes **5** and **8**, with fewer OEt groups, undergo rapid thermal decomposition that is almost complete within 0.5 h. This contrasts with the reactions of **4** and **6**, which require 24 h or longer for complete consumption of the complexes. The reactions of **4**−**8** obey first-order kinetics. Figure 5b shows the first-order plots of the reactions at 60 °C. The observed rate constants increase in the order **4** (1.04×10^{-5} s^{-1}) < **6** (2.01×10^{-5} s^{-1}) < **7** (5.59×10^{-4} s^{-1}) < **5** (2.9×10^{-3} s^{-1}) ≅ **8** (3.7×10^{-3} s^{-1}). The complexes having fewer alkoxy substituents on Si undergo much faster decomposition. Reductive elimination of the $ClSiR_3$ is easier than that of $ISiR_3$ from the Rh complex with the same alkoxy-silyl ligand.



(4)

5-8

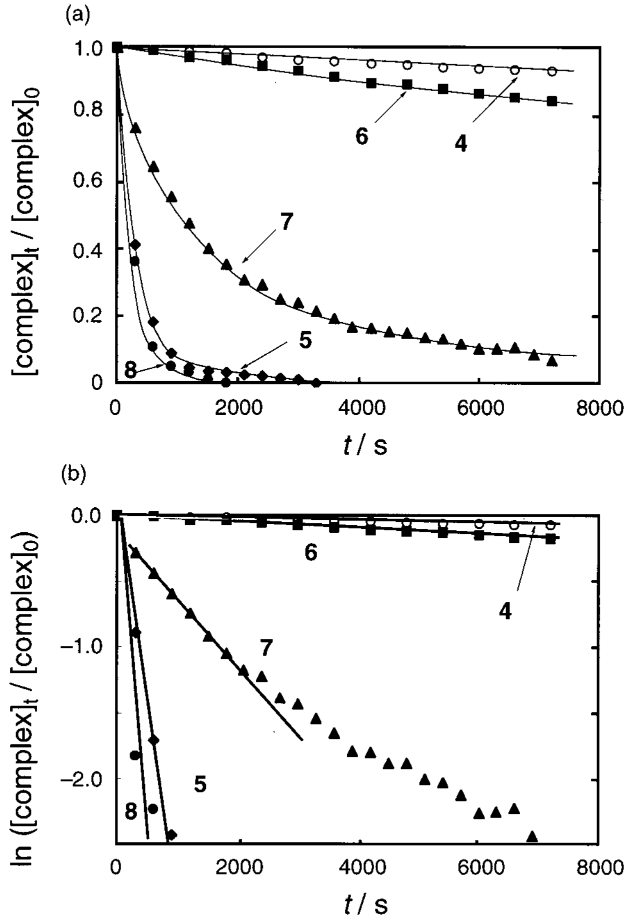


Figure 5. (a) Time−yield curve and (b) first-order polts of thermal decomposition of **4**−**8** at 60 °C in benzene-d_6.

Discussion

The silylrhodium(III) complexes in this study have similar structures but different reactivities toward coupling of the halo and silyl ligands, a process that depends on the kind of halo and silyl ligands. They have meridional arrangement of halo, silyl, and hydrido ligands in square-pyramidal coordination with the silyl ligand in the apical position; the coordination is quite similar to that in $RhCl(H)(SiAr_3)\{P(i\text{-}Pr)_3\}_2$. The structure is the thermodynamically favored one among the possible structures because the complexes have a flexible and labile pentacoordinated Rh center and because the complexes are equilibrated to halorhodium(I) complexes via rapid reductive elimination of triorganosilane and its reoxidative addition. A theoretical study on oxidative addition of SiH_4 to $RhCl(PH_3)_2$ suggests a greater stability of the structure $RhCl(H)(SiH_3)(PH_3)_2$ with the Cl and silyl ligands with much larger Si−Rh−Cl angles (135.8−136.6°) than the structures of **1**−**8**.[27] The calculated and observed stable pentacoordinated structures differ depending on the substituents at the Si and P centers, suggesting a small difference in the stability of the two structures.

The geometry of the Rh(III) complexes with the silyl ligand in cis position to the hydrido ligand and halo ligand in this study allows direct coupling of the hydrido and silyl ligands, and that of the halo and silyl ligands. The pentacoordinate complexes $RhCl(H)(SiAr_3)\{P(i\text{-}$

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[27] Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1993**, *115*, 6883.

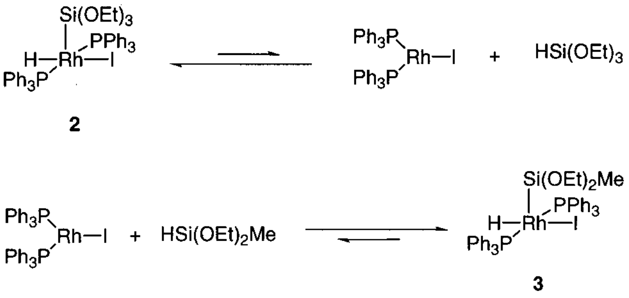
Pr)$_3$}$_2$, without alkoxy groups on Si, undergo reductive elimination of $ClSiAr_3$ even at room temperature. The hydridorhodium(I) product is soon captured by the rhodium(III) complex to form bimetallic rhodium products such as {P(*i*-Pr)$_3$}(Ar_3Si)HRh(μ-H)(μ-Cl)RhH($SiAr_3$){P(*i*-Pr)$_3$}. In sharp contrast, chlororhodium complexes **5**−**8** with OEt or $OSiMe_3$ groups on the Si center are stable at room temperature. Thermally induced elimination of $ClSiMe_n(OR)_{3-n}$ from **5**−**8** takes place at 60 °C. The reaction rates vary significantly depending on the number of alkoxy groups on the Si center; the observed rate constants decrease in the order **5** ≅ **8** > **7** > **6** with an increase of the number of alkoxy groups. The reaction giving $ClSi(OEt)_3$ from **6** at 60 °C proceeds at a slightly faster rate than the thermal reaction of **4** to give $ISiMe_2(OEt)$ at the same temperature. Other iodo complexes **2** and **3** are stable even at 60 °C. These results indicate that introduction of OEt (or $OSiMe_3$) groups on Si retards the reductive elimination due to the stable Rh−Si bond and that coupling of chloro(triorgano)silane from the Rh(III) center is more facile than that of iodo(triorganosilane). A markedly different thermal stability was observed between iodo complexes **1**−**4** and chloro complexes **5**−**8** toward coupling of the halo and silyl ligands.

Reductive elimination of haloalkane via concerted coupling of the halo and alkyl (or aryl) ligands is not common in the chemistry of alkyltransition metal complexes. On the other hand, the concerted intramolecular coupling of the chloro and organosilyl ligands of the Rh(III) complexes takes place easily. A series of $RhCl(H)(SiR_3)(PR'_3)_n$ (R = Ar, H; PR'_3 = PMe_3, P(*i*-Pr)$_3$) type complexes form $ClSiR_3$ smoothly at room temperature only when the Cl and silyl ligands are in mutually cis positions in a square-pyramidal or octahedral coordination. Coupling of Cl and SiR_3 in Ir(III) and Pt(IV) complexes with chloro and silyl ligands was previously proposed in the reaction of an excess of organosilanes with chloro complexes of Ir(I) and Pt(II) by Chalk and Harrod.[19]

The Rh−Si bonds of **2** and **6** are shorter than that of **1** and than almost all the Rh−Si bond reported so far. Previously we reported that the Rh−Si bond of RhCl(H){Si(C≡CPh)$_3$}{P(*i*-Pr)$_3$}$_2$ was much shorter than that of RhCl(H)($SiAr_3$){P(*i*-Pr)$_3$}$_2$, which suggests a significant effect of the electron-withdrawing alkynyl group on the Si−Rh bond distance. Crystallographic studies and NMR spectroscopic studies of the complexes revealed a shortening of the Rh−Si bond and an increase in *J*(RhSi) caused by introduction of the alkoxy group at Si. These results indicate that the OR groups render the σ-bond between Rh and Si more stable. The smaller magnitude of $\delta\Delta$ values of the complexes with larger OEt groups of the Si center seems to suggest a strengthening of the covalent σ-coordination bond.

NMR measurement of complex **2** with various organosilanes gave thermodynamic parameters of complexes **1**−**4** via reductive elimination of $HSiMe_n(OR)_{3-n}$, followed by oxidative addition of organosilane (Scheme 2). The $\Delta G°$ or $\Delta H°$ do not correlate directly with the number of OR groups of the complexes nor with relative stability of the Rh−Si bonds that are estimated based on the rate constants of coupling of complexes **5**−**8** or *J*(RhSi) values. Since the magnitude of $T\Delta S°$ is larger than $\Delta H°$ in many of the reactions, the obtained thermodynamic parameters do not provide important information about relative stability of the Rh−Si bond.

Scheme 2



Experimental Section

General Procedures. All manipulations were carried out under a nitrogen or an argon atmosphere using standard Schlenk techniques. Hexane and toluene were distilled from sodium and benzophenone prior to use or purchased from Kanto Chemicals Co. Ltd. $RhCl(PPh_3)_3$ and $RhI(PPh_3)_3$ were prepared according to published procedures.[28] NMR spectra (^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$, and $^{31}P\{^1H\}$) were recorded on JEOL EX-400 or Varian Mercury 300 spectrometers. Residual peaks of solvent were used as the reference for ^1H NMR (benzene-*d*$_6$, δ 7.15; dichloromethane-*d*$_2$, δ 5.32; toluene-*d*$_8$, δ 2.09). $^{13}C\{^1H\}$ NMR signals were referenced with the solvent signals, while 85% H_3PO_4 (δ 0) and tetramethylsilane (δ 0) were used as an external standard for $^{31}P\{^1H\}$ and $^{29}Si\{^1H\}$ NMR measurements, respectively. The IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer in KBr. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder.

Preparation of Complexes 1−**8.** To a toluene (25 mL) dispersion of $RhI(PPh_3)_3$ (800 mg, 0.80 mmol) was added $HSiMe_2OSiMe_3$ (157 μL, 0.80 mmol) at room temperature. The dispersed reddish brown solid was gradually dissolved on stirring to give a pale yellow solution. After 2 h, the solution was concentrated and 30 mL of hexane was added to give a pale yellow precipitate; the latter was collected by filtration, washed with hexane (15 mL x 3 times), and dried in vacuo to give **1** as a pale yellow solid (683 mg, 88%). Recrystallization from toluene/hexane afforded pale yellow crystals suitable for X-ray crystallography. Complexes **2**−**4** and **6** were prepared analogously.

Complexes **5**, **7**, and **8** were prepared analogously, but the products were isolated quickly after the reaction for 1 h in order to avoid decomposition of the complexes.

Equilibrium Constants of the Reaction of 2 with Triorganosilanes. To a toluene-*d*$_8$ (0.7 mL) solution of **2** (10 mg, 1.1×10^{-2} mmol) in an NMR sample tube were added $HSi(OEt)_2Me$ (16.7 μL, 10×10^{-2} mmol) and $HSi(OEt)_3$ (18.4 μL, 9.8×10^{-2} mmol). The tube was sealed and heated at 50 °C for 2 h in an oil bath. Subsequently it was set in an NMR probe and kept at fixed temperatures (278, 288, 298, 308, and 318 K) for 30 min. The equilibrium constants between **2** and **3** were determined by comparison of the ^1H NMR peak areas of the Si-H hydrogen signals of the two hydrosilanes (δ 4.78 for *H*Si(OEt)$_2$Me and δ 4.52 for *H*Si(OEt)$_3$) and the Rh-H hydrogen signals of the complexes (δ −10.99 for **2** and δ −11.16 for **3**). The equilibrium constants at each temperature in the reaction of **2** with various hydrosilanes are shown in Table 6.

Thermal Reactions of 4−**8.** A solution of **6** (19.4 mg, 0.036 mmol) in carefully dried and digassed benzene-*d*$_6$ (0.6 mL) was

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[28] Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711.

Table 7. Crystal Data and Details of the Structure Refinement of 1, 2, and 6

	1	**2**	**6**
formula	$C_{41}H_{82}IOP_2Si_2Rh$	$C_{42}H_{46}IO_3P_2SiRh$	$C_{42}H_{46}ClO_3P_2SiRh{\cdot}C_7H_8$
mol wt	939.03	918.67	919.36
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	17.838(5)	13.171(3)	13.053(3)
b (Å)	18.828(4)	13.706(3)	18.541(4)
c (Å)	15.023(3)	12.637(2)	10.173(3)
α (deg)	104.37(2)	112.62(1)	101.35(2)
β (deg)	101.63(2)	101.99(2)	92.20(2)
γ (deg)	115.85(2)	88.50(2)	103.58(2)
V (Å^3)	4112(2)	2056.2(8)	2337(1)
Z	4	2	2
μ (mm^{-1})	1.334	1.308	0.555
F(000)	1968	928	956
D_{calcd} (g cm^{-3})	1.517	1.484	1.306
cryst size	0.25 × 0.20 × 0.13	0.50 × 0.30 × 0.05	0.45 × 0.45 × 0.05
2θ range (deg)	5.0−50.0	5.0−55.0	5.0−55.0
no. of unique reflns	10 877	9421	10 709
no. of used reflns	6177	5320	5229
no. of variables	873	455	483
R	0.036	0.040	0.058
R_w[a]	0.026	0.030	0.057

[a] Weighting scheme $[\sigma(F_o)^2]^{-1}$.

prepared in an NMR tube under argon. The sample was degassed and sealed. Heating the sample at 60 °C for 24 h caused consumption of the complex and formation of ClSi(OEt)$_3$ (80%). Reactions of **4**, **5**, **7**, and **8** were carried out in an NMR sample tube under Ar. Heating a benzene-d_6 solution of **5** (55 min), **7** (3 h), and **8** (0.5 h) at 60 °C gave ClSiMe$_2$OSiMe$_3$ (76%), ClSi(OEt)$_2$Me (66%), and ClSi(OEt)Me$_2$ (61%), respectively. These products were characterized by comparison of the NMR peak positions with the authentic samples. Byproducts were also observed in the reaction mixtures in 7−13% yields. They did not give satisfactory GC−mass data and were not characterized unambiguously, although they may be tentatively assigned to the corresponding siloxanes formed via condensation of the above products during the reaction.

Kinetic measurement of the reactions was carried out by ^{1}H NMR spectra using the solution prepared as above.

X-ray Diffraction. Single crystals of **1**, **2**, and **6** suitable for X-ray diffraction studies were grown from toluene−hexane. Crystallographic data and details of refinement are summarized in Table 7. The crystals were sealed in glass capillary tubes and mounted on a Rigaku AFC-5R or AFC-7R automated four-cycle diffractometer. Intensities were collected for Lorentz and by using diffractometer and $\omega-2\theta$ scan methods, and an empirical absorption correction (ψ scan) was applied. The intensities of three standard reflections, measured every 150 reflections, were monitored throughout the data collection. Calculations were carried out using the program package teXsan for Windows. The structures were solved by the Patterson method. A full matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. All non-hydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters.[29]

Acknowledgment. This work was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, Technology and Culture of Japan.

Supporting Information Available: Table of crystallographic data and complete tables of non-hydrogen and selected hydrogen parameters, bond lengths and angles, calculated hydrogen atom parameters, anisotropic thermal parameters, and intermolecular contacts for **1**, **2**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010862O

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(29) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.