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Thermal Isomerization of *mer*-[RhH(SAr)(SiHAr′$_2$)(PMe$_3$)$_3$] to *fac*-[RhH$_2$\{SiAr′$_2$(SAr)\}(PMe$_3$)$_3$] Involving Thiolato Group Transfer from Rh to Si

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Heating of a benzene or toluene solution of *mer*-[RhH(SAr)(SiHAr′$_2$)(PMe$_3$)$_3$] (Ar = C$_6$H$_5$, C$_6$H$_4$Me-*p*, C$_6$H$_4$OMe-*p*; Ar′ = C$_6$H$_5$, C$_6$H$_4$Me-*p*, C$_6$H$_4$F-*p*, C$_6$H$_4$CF$_3$-*p*) at 30—50 °C gives *fac*-[RhH$_2$\{SiAr′$_2$(SAr)\}(PMe$_3$)$_3$] quantitatively through thiolato group transfer from Rh to Si. X-Ray structural analysis of *fac*-[RhH$_2$\{SiPh$_2$(SPh)\}(PMe$_3$)$_3$] reveals octahedral coordination with three PMe$_3$ ligands at facial coordination sites, while the ^{1}H NMR spectra show the presence of two equivalent hydrido ligands. The other Rh complexes are isolated or characterized in situ by means of NMR spectroscopy. The reaction of *mer*-[RhH(SC$_6$H$_4$Me-*p*)(SiHPh$_2$)(PMe$_3$)$_3$] to form the Rh complex obeys first-order kinetics with the kinetic parameters: $\Delta G^{\ddagger}$ = 98.6 kJ mol^{-1}, $\Delta H^{\ddagger}$ = 94.9 kJ mol^{-1}, and $\Delta S^{\ddagger}$ = −12 J mol^{-1} deg^{-1} at 298 K. The rate constants of the reaction of *mer*-[RhH(SC$_6$H$_4$X-*p*)(SiHPh$_2$)(PMe$_3$)$_3$] (X = H, Me, OMe) increase with increasing Hammett constant σ_p of substituent X. The substituent of the diarylsilyl ligand of *mer*-[RhH(SC$_6$H$_4$X-*p*)\{SiH(C$_6$H$_4$Y-*p*)$_2$\}(PMe$_3$)$_3$] (X = Me or OMe; Y = H, Me, F, CF$_3$) also influences the reaction rate constant, while the degree of enhancement is not directly related to the electron donating or withdrawing ability of substituent Y. Possible reaction mechanisms are discussed based on these results.

Transition metal complex-catalyzed dehydrogenative condensation of organosilanes with alcohols, thiols, and amines to form Si–O,[1] Si–S,[2] and Si–N[3] bonds has attracted considerable attention in view of the synthesis of Si-containing polymers or precursors of inorganic ceramics. The coupling of organosilyl group with alkoxido ligand bonded to transition metal has recently been investigated by several research groups. Luo and Crabtree found high catalytic performance of a cationic iridium complex for silane alcoholysis and proposed a mechanism involving nucleophilic attack by alcohol on an Ir(η^2-HSiR$_3$) intermediate based on the kinetic results.[4] Caulton reported details of the reaction of [Cp*Ru(OCH$_2$CF$_3$)(PR$_3$)] with HSiR′$_3$ in a 1 : 2 molar ratio to afford a mixture of [Cp*Ru(H)$_2$(SiR′$_3$)(PR$_3$)] and R′$_3$SiOCH$_2$CF$_3$.[5] Rapid formation of the alkoxysilane indicates facile coupling of the fluoroalkoxido and tertiary silyl ligands from an intermediate [Cp*Ru(H)(SiR′$_3$)(OCH$_2$CF$_3$)(PR$_3$)]. The silylation of the bridging alkoxido group bonded to Ru and Ir dinuclear complexes was also reported.[6] The reaction of [Cp*IrMe(OTf)(PMe$_3$)] with triorganosilane, reported by Bergman and coworkers, led to not only Si–O bond formation but also Si–C bond cleavage to give [Cp*Ir(R)\{SiR$_2$(OTf)\}(PMe$_3$)] type complexes.[7] Diphenylsilane reacted with [Ir(OAc)L$_2$(PR$_3$)] to give [Ir(H)$_2$\{Si(OAc)Ph$_2$\}L$_2$(PR$_3$)] (L = CO or 0.5 diene) as reported by Esteruelas and Werner, who proposed two independent reaction mechanisms, one involving reductive elimination of HSiPh$_2$(OAc) from intermediate [Ir(OAc)L$_2$(H)(SiHPh$_2$)(PR$_3$)] and the other involving an intermediate Ir(III) complex containing a diphenylsilylene ligand.[8]

The reaction of organosilane with thiolato transition metal complexes has attracted less attention although it would be of interest in relation to the transition metal-promoted dehydrogenative coupling of organosilane with thiol. [RhCl(PPh$_3$)$_3$] catalyzed dehydrogenative condensation of organosilanes with thiols under mild conditions[2] has tempted us to examine the reaction of organosilane with thiolatorhodium complexes with a PR$_3$ ligand. Previously, we prepared [Rh(SAr)(PMe$_3$)$_3$] type complexes that undergo facile oxidative addition of organic molecules including di- and triorganosilanes.[9] Here we report the preparation of *mer*-[RhH(SAr)(SiHAr′$_2$)(PMe$_3$)$_3$] from oxidative addition of diarylsilane to the Rh(I) complexes as well as their thermal reaction resulting in Si–S bond formation from the diarylsilyl and thiolato ligands. Part of this study has been reported in a preliminary form.[10]

Results and Discussion

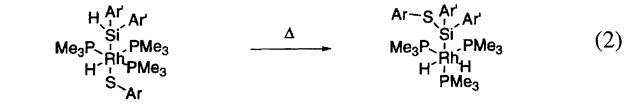
Preparation and Thermal Reaction of *mer*-[RhH(SAr)(SiHAr′$_2$)(PMe$_3$)$_3$]. Complexes *mer*-[RhH(SAr)(SiHAr′$_2$)(PMe$_3$)$_3$] were prepared by oxidative addition of diarylsilane to [Rh(SAr)(PMe$_3$)$_3$], as shown in Eq. 1.

(1)

1a: Ar = C_6H_5, Ar' = C_6H_5;
1b: Ar = C_6H_5, Ar' = C_6H_4Me-*p*;
2a: Ar = C_6H_4OMe-*p*, Ar' = C_6H_5;
2b: Ar = C_6H_4OMe-*p*, Ar' = C_6H_4Me-*p*;
2c: Ar = C_6H_4OMe-*p*, Ar' = C_6H_4F-*p*;
2d: Ar = C_6H_4OMe-*p*, Ar' = $C_6H_4CF_3$-*p*;
3a: Ar = C_6H_4Me-*p*, Ar' = C_6H_5;
3c: Ar = C_6H_4Me-*p*, Ar' = C_6H_4F-*p*;
3d: Ar = C_6H_4Me-*p*, Ar' = $C_6H_4CF_3$-*p*

Not only previously prepared **1a**, **1b**, **2a**, **3a**, and **3c**[9d] but also new complexes **2b**, **2c**, **2d**, and **3d** exhibit NMR signals that are consistent with the octahedral coordination around the Rh center that is bonded to diarylsilyl and arenethiolato ligands at mutually trans positions. Deuterium-labeled complexes [Rh(SC_6H_4OMe-*p*)D($SiDPh_2$)(PMe_3)$_3$] (**2a**-d_2) and [Rh(SC_6H_4Me-*p*)D($SiDPh_2$)(PMe_3)$_3$] (**3a**-d_2) were obtained from the analogous reaction of Ph_2SiD_2 with [Rh(SC_6H_4X-*p*)(PMe_3)$_3$] (X = Me, OMe).

Heating of a benzene or toluene solution of **1a**, **2a**, and **3a** at 30—50 °C leads to the conversion of the complexes to *fac*-[RhH_2{$SiPh_2$(SAr)}(PMe_3)$_3$] (**4a**: Ar = C_6H_5, **5a**: Ar = C_6H_4OMe-*p*, **6a**: Ar = C_6H_4Me-*p*), as shown in Eq. 2. The reaction cleaves the Si–H and Rh–S bonds of the starting complex and forms new Si–S and Rh–H bonds. No products other than the above complexes were found in the reaction mixture.



(2)

1a: Ar = C_6H_5, Ar' = C_6H_5;
1b: Ar = C_6H_5, Ar' = C_6H_4Me-*p*;
2a: Ar = C_6H_4OMe-*p*, Ar' = C_6H_5;
2b: Ar = C_6H_4OMe-*p*, Ar' = C_6H_4Me-*p*;
2c: Ar = C_6H_4OMe-*p*, Ar' = C_6H_4F-*p*;
2d: Ar = C_6H_4OMe-*p*, Ar' = $C_6H_4CF_3$-*p*;
3a: Ar = C_6H_4Me-*p*, Ar' = C_6H_5;
3c: Ar = C_6H_4Me-*p*, Ar' = C_6H_4F-*p*;
3d: Ar = C_6H_4Me-*p*, Ar' = $C_6H_4CF_3$-*p*

4a: Ar = C_6H_5, Ar' = C_6H_5;
4b: Ar = C_6H_5, Ar' = C_6H_4Me-*p*;
5a: Ar = C_6H_4OMe-*p*, Ar' = C_6H_5;
5b: Ar = C_6H_4OMe-*p*, Ar' = C_6H_4Me-*p*;
5c: Ar = C_6H_4OMe-*p*, Ar' = C_6H_4F-*p*;
5d: Ar = C_6H_4OMe-*p*, Ar' = $C_6H_4CF_3$-*p*;
6a: Ar = C_6H_4Me-*p*, Ar' = C_6H_5;
6c: Ar = C_6H_4Me-*p*, Ar' = C_6H_4F-*p*;
6d: Ar = C_6H_4Me-*p*, Ar' = $C_6H_4CF_3$-*p*

Recrystallization of **4a** from acetone led to growth of colorless crystals (form I) and pale yellow crystals (form II). Figure 1 shows the molecular structure of **4a** (form I), which is similar to that of form II in our preliminary report.[10,11] The molecule contains an octahedral coordination around the Rh center which is bonded to three facial PMe_3 and a benzenethiolato(diphenyl)silyl ligand. The position of a hydrido ligand cannot be determined by differential Fourier technique, although the presence of two equivalent hydrido ligands is confirmed by the ^{1}H NMR spectrum. The ^{1}H and ^{31}P{^{1}H} NMR spectra of **4a**, **5a**, and **6a** are consistent with the octahedral structure that has two mutually *cis* hydrido and three facial PMe_3 ligands. The ^{1}H NMR signal of the hydrido appears as a multiplet with a large coupling constant (J(HP) = 117 Hz) due to the P nucleus that is positioned trans to the hydrido. The ^{1}H NMR peak pattern of the hydrido signals as well as the ^{31}P{^{1}H} NMR peak positions and coupling constants are very similar to those of *fac*-[RhH_2($SiClPh_2$)(PMe_3)$_3$] which was previously characterized by X-ray analysis.[12] An analogous Ir complex, *fac*-[IrH_2(SiR_3)(PMe_3)$_3$], which has two hydrido, a SiR_3 and

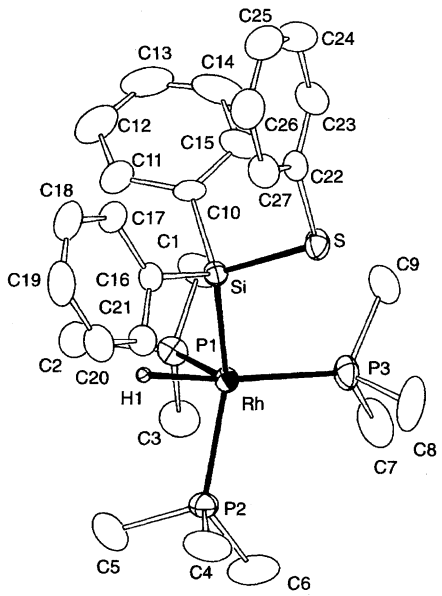


Fig. 1. A perspective drawing of complex **4a** (form I). Selected bond distances (Å) and angles (°): Rh–P1 2.342(1), Rh–P2 2.337(1), Rh–P3 2.330(1), Rh–Si 2.336(1), Rh–H1 1.67(6), Si–S 2.224(2), Si–C10 1.882(4), Si–C16 1.909(4), P1–Rh–P2 97.16(4), P1–Rh–P3 98.32(5), P1–Rh–Si 103.48(4), P1–Rh–H1 87(2), P2–Rh–P3 102.51(5), P2–Rh–Si 145.89(4), P2–Rh–H1 84(2), P3–Rh–Si 101.03(4), P3–Rh–H1 171(4), Si–Rh–H1 70(2), Si–S–C22 104.7(1). One of the two hydrido ligands is not located.

three facial PMe_3 ligands has been similarly characterized.[13] The structure contains hydrido and silyl ligands with large *trans* influence at mutually *cis* positions and seems to be more thermodynamically favored than the isomer with three PMe_3 at meridional coordination sites.

Thermal reaction of **1b**, **2b**—**d**, **3c**, and **3d** was carried out in NMR tubes. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the reaction mixture showed selective formation of the arenethiolato(diaryl)silyl(dihydrido)rhodium complexes: **4b**, **5b**—**d**, **6c**, and **6d**. The reaction of **3a** to give **6a** was followed by a decrease in the ^{1}H NMR signal intensity of the methyl hydrogens of the thiolato ligand. Figure 2 shows linear first-order plots of the reaction in the temperature range 30—50 °C, indicating the first-order kinetics to [**3a**]. The kinetic parameters are obtained from the temperature dependence of the rate constants as $\Delta G^{\ddagger}$ = 98.6 kJ mol^{-1}, $\Delta H^{\ddagger}$ = 94.9 kJ mol^{-1}, and $\Delta S^{\ddagger}$ = −12 J mol^{-1} deg^{-1} at 298 K. Table 1 summarizes the rate constants of the reactions of all the complexes examined. The order of the rate constants at 313 K: **2a** > **3a** > **1a** suggests that the presence of an electron-donating para-substituent of arenethiolato ligand enhances the thermal reaction. The differences in rate constants among **2a**—**2d** and among **3a**, **3c**, and **3d** mean that the para-substituent attached to the diarylsilyl ligand also influences the reaction rate. The order of enhancement by the substituents: F > H > Me > CF_3 does not correlate directly to the Hammett constant σ_p or to any other substituent constants. The rate constants of the thermal reaction of **2a**—d_2 and of **3a**—d_2 are smaller than those

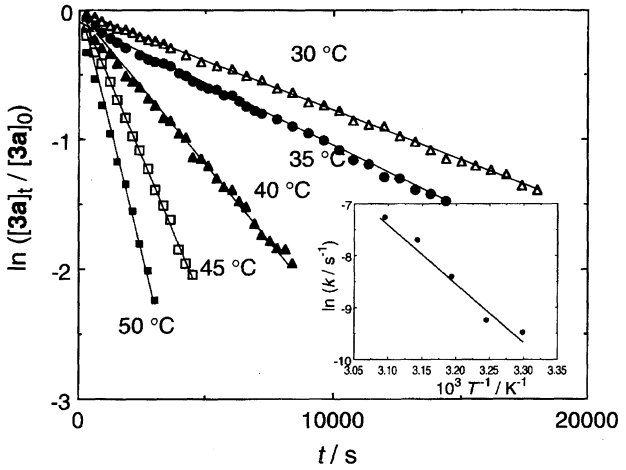


Fig. 2. First-order plots of reaction of **3a** to **6a** obtained from change of ^{1}H NMR peak intensity of Me hydrogens of the thiolato ligand of **3a**. The Arrhenius plots are shown in inset.

Table 1. Kinetic Results of Thermal Reaction of *mer*-[RhH(SAr)(SiHAr′$_2$)(PMe$_3$)$_3$]

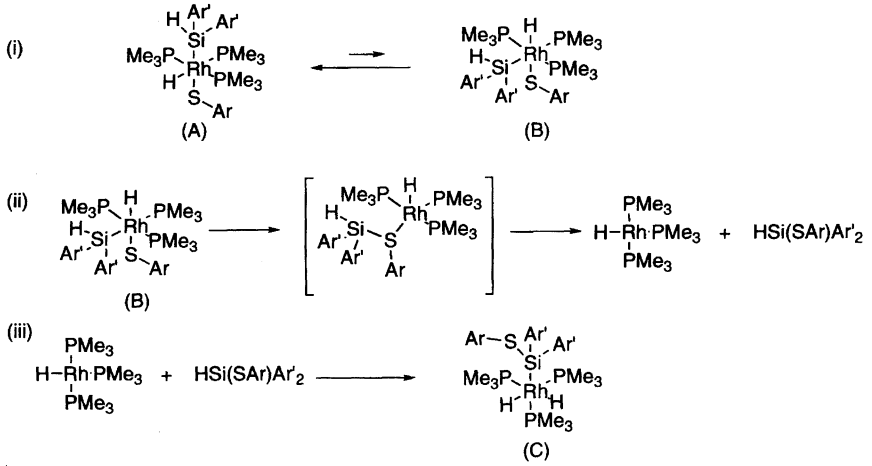
	Complex		Temp	k
	Ar	Ar′	K	s^{-1}
1a	C_6H_5	C_6H_5	313	1.5×10^{-4} a)
2a	C_6H_4OMe-*p*	C_6H_5	313	3.23×10^{-4}
2a-d_2	C_6H_4OMe-*p*	C_6H_5	313	2.65×10^{-4}
2b	C_6H_4OMe-*p*	C_6H_4Me-*p*	313	2.43×10^{-4}
2c	C_6H_4OMe-*p*	C_6H_4F-*p*	313	4.49×10^{-4}
2d	C_6H_4OMe-*p*	$C_6H_4CF_3$-*p*	313	1.61×10^{-4}
3a	C_6H_4Me-*p*	C_6H_5	303	7.63×10^{-5}
			308	9.70×10^{-5}
			313	2.24×10^{-4}
			318	4.52×10^{-4}
			323	7.06×10^{-4}
3a-d_2	C_6H_4Me-*p*	C_6H_5	313	1.77×10^{-4}
3c	C_6H_4Me-*p*	C_6H_4F-*p*	313	3.30×10^{-4}
3d	C_6H_4Me-*p*	$C_6H_4CF_3$-*p*	313	1.56×10^{-4}

a) The rate constant is less precise than the others because the reaction was monitored using $^{31}P\{^1H\}$ NMR signals.

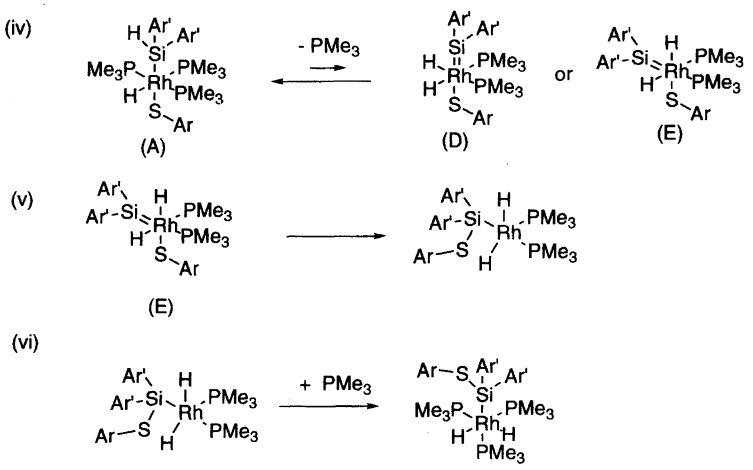
of non-deuterated complexes. The above reactions give a single product, whereas thermal reaction of *mer*-[RhCl(H)(SiHPh$_2$)(PMe$_3$)$_3$] proceeds more slowly to give a mixture of *fac*-[RhH$_2$(SiClPh$_2$)(PMe$_3$)$_3$] having structures similar to **4a**—**6d** and *fac*-[RhCl(H)(SiClPh$_2$)(PMe$_3$)$_3$].[12] The latter product is likely formed through an intermolecular reaction of the Cl and SiHPh$_2$ groups.

Schemes 1 and 2 illustrate reaction pathways that rationalize the transfer of thiolato group from Rh center to Si leading to formation of *fac*-[RhH$_2${SiAr′$_2$(SAr)}(PMe$_3$)$_3$]. According to Scheme 1, complex (A) undergoes isomerization to (B) with the diarylsilyl and hydrido ligands at cis position (i). Complex (B) releases HSi(SAr)(Ar′)$_2$ through intramolecular reductive elimination (ii) and the resulting [RhH(PMe$_3$)$_3$] should undergo reoxidative addition of its Si–H bond (iii). Intramolecular coupling of diarylsilyl and thiolato ligands at mutually trans positions is not feasible and requires trans-cis isomerization at the initial stage of the reaction. A plausible pathway of the isomerization involves reductive elimination of H$_2$SiAr$_2$ from (A) followed by its oxidative addition to [Rh(SAr)(PMe$_3$)$_3$] to regenerate (A) or generate (B) because *mer*-[RhCl(H)(SiHAr$_2$)(PMe$_3$)$_3$] with a similar structure to (A) undergoes the rapid reductive elimination of H$_2$SiAr$_2$ and its reoxidative addition and because *mer*-[RhCl(H){Si(C$_6$H$_4$CF$_3$)$_3$}(PMe$_3$)$_3$] with a coordination similar to (B) was structurally characterized.[12,14]

According to Scheme 2, the Rh complex (A) undergoes loss of a PMe$_3$ ligand and α-hydrogen elimination of diarylsilyl ligand to give diarylsilylene group coordinated Rh(III) intermediates (D) and (E) (iv). Then the silylene group of (E) is attacked by the thiolato ligand to form a product containing a diaryl(thiolato)silyl ligand (v). α-Hydrogen elimination from diorganosilyl group bonded to transition metal has been postulated as the crucial step in several reactions of organosilane catalyzed by transition metal complexes.[15] Complexes with a diorganosilylene ligand have been isolated recently and readily react with alkoxido or amido group to give the base stabilized silylene complexes.[16] The reaction pathway in Scheme 2 requires pre-dissociation of a PMe$_3$



Scheme 1.



Scheme 2.

ligand in order to generate the silylene-coordinated intermediate complex. The addition of PMe_3 to the reaction mixture was examined in order to observe the effect of free PMe_3 on the reaction rate. The low boiling point of PMe_3 did not allow estimation of the effect of [PMe_3] on the rate constant.[17]

The experimental results obtained in the present study are consistent with both of the pathways shown in Schemes 1 and 2. A small negative activation entropy of the thiolato group transfer reaction excludes the pathway involving dissociation of PMe_3 as the rate-determining step. In Scheme 1, such a small negative activation entropy in the reductive elimination of $HSi(SAr)Ar'_2$ from (B) (ii) suggests the presence of an intermediate $[RhH\{SiH(SAr)Ar'_2\}(PMe_3)_3]$ having coordination of the S atom of the diaryl(thiolato)silane to the Rh center. Reductive elimination of methane from $[(Cp^*)_2W(H)Me]$ showed a small activation entropy, which was attributed to the formation of an intermediate methane-coordinated tungsten complex after the transition state.[18] The small negative activation entropy in the pathway in Scheme 2 can be rationalized by assuming the rate-determining step in the nucleophilic attack of the thiolato ligand on the diarylsilylene group (v).

Rate constants of the thermal reactions of **2a** and **3a** are larger than those of deuterated complexes **2a**-d_2 and **3a**-d_2 with an apparent kinetic isotope effect $k_{HH}/k_{DD} = 1.22$ and 1.27, respectively, at 40 °C. The isotope effect influences both pre-equilibrium ((i) in Scheme 1 and (iv) in Scheme 2) and the rate-determining step ((ii) in Scheme 1 and (v) in Scheme 2) of the reaction. Detailed study on oxidative addition of $HSiR_3$ and $DSiR_3$ to Ta–Ir(I) heterobimetallic complex and the reverse reductive elimination from the resulting Ta–Ir(III) complex afforded a deuterium isotope effect, $k_H/k_D = 1.45$, for the reductive elimination of a triorganosilane. The small normal isotope effect results from compensation of the normal primary effect on the reductive elimination and the reverse secondary effect on the oxidative addition-reductive elimination equilibrium constant.[19] Thus the kinetic results in the present study indicate the pathway in Scheme 1 or that in Scheme 2, although it is not feasible to favor or disfavor one of the two plausible pathways for the multi-step reaction.

The present study has shown the preparation of Rh complexes containing both diarylsilyl and arenethiolato ligands. The trans coordination of the silyl and thiolate ligands serves to stabilize the complex by preventing their direct coupling. Gentle heating of the complexes results in selective Si–S bond formation to give the Rh complex with a diaryl(thiolato)silyl ligand. The reaction occurs under milder conditions and gives the product more cleanly than similar reaction of *mer*-$[RhCl(H)(SiHAr_2)(PMe_3)_3]$ giving *fac*-$[RhH_2(SiClAr_2)(PMe_3)_3]$. The smooth coupling of thiolato and silyl groups bonded to the Rh center seems to be closely related to the mechanism of dehydrocoupling of thiol and organosilane catalyzed by Rh complexes.

Experimental

General Considerations, Measurement, and Materials. Manipulations of Rh complexes were carried out under nitrogen or argon using standard Schlenk techniques. Complexes **1a**, **1b**, **2a**, **3a**, **3c**, $[Rh(SAr)(PMe_3)_3]$, and diarylsilanes were prepared according to the literature.[9,20] NMR spectra (^1H and ^{31}P) were recorded on JEOL EX-90 or EX-400 spectrometers. $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. Elemental analyses were carried out by Yanaco MT-5 CHN autocorder and Yazawa Halogen & Sulfur Analyzer.

Preparation of 2b, 2c, 2d, and 3d. To a hexane (25 cm^3) solution of $[Rh(SC_6H_4OMe\text{-}p)(PMe_3)_3]$ (273 mg, 0.58 mmol) was added a hexane (3 cm^3) solution of $H_2Si(C_6H_4Me\text{-}p)_2$ (128 mg, 0.60 mmol) at room temperature. The initial orange solution became yellow on stirring. After 3 h, a colorless solid was precipitated from the solution. The solid product was collected by filtration, washed with a small amount of hexane and dried in vacuo to give **2b** as colorless solid (283 mg, 72%). IR (KBr) 2086 (ν(SiH)), 1974 (ν(RhH)), 1230 cm^{-1} (ν(CO)); ^1H NMR (C_6D_6) $\delta = -8.94$ (ddt, 1H, RhH, J = 155, 18, 18, and 16 Hz), 1.02 (d, 9H, $P(CH_3)_3$, J = 7 Hz), 1.26 (apparent triplet due to virtual coupling, 18H, $P(CH_3)_3$), 2.15 (s, 6H, $C_6H_4CH_3$), 3.41 (s, 3H, $C_6H_4OCH_3$), 5.51 (dt, 1H, SiH, J = 11, 9, 9, and 9 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6) $\delta = -12.0$ (dd, J(RhP) = 98 Hz, J(PP) = 32 Hz), −27.7 (dt, J(RhP) = 91 Hz, J(PP) = 32 Hz). Found: C, 52.90; H, 7.71; S, 5.22%. Calcd for $C_{30}H_{50}OP_3SSiRh$: C, 52.78; H, 7.38; S, 4.70%.

Complexes **2c**, **2d**, **3d**, **2a**-d_2, and **3a**-d_2 were prepared analogously.

2c: Yield 65%; IR (KBr) 2026 (ν(SiH)), 1233 cm^{-1} (ν(CO));

^{1}H NMR (C_6D_6) δ = −9.16 (ddt, 1H, RhH, J = 153, 18, 18, and 16 Hz), 0.99 (d, 9H, $P(CH_3)_3$, J = 7 Hz), 1.16 (apparent triplet due to virtual coupling, 18H, $P(CH_3)_3$), 3.40 (s, 3H, OCH_3), 5.36 (dt, 1H, SiH, J(PH) = J(RhH) = 10 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6) δ = −12.3 (dd, J(RhP) = 97 Hz, J(PP) = 32 Hz), −28.0 (dt, J(RhP) = 91 Hz, J(PP) = 32 Hz). Found: C, 48.86; H, 6.69%. Calcd for $C_{28}H_{44}OF_2P_3SSiRh$: C, 48.70; H, 6.42%.

2d: (obtained in a hexane-solvated form): Yield 79%; IR (KBr) 2044 (ν(SiH)), 1999 (ν(RhH)), 1227 cm^{-1} (ν(CO)); ^{1}H NMR (C_6D_6) δ = −9.01 (ddt, 1H, RhH, J = 153, 18, 18, and 15 Hz), 0.99 (d, 9H, $P(CH_3)_3$, J = 7 Hz), 1.22 (apparent triplet due to virtual coupling, 18H, $P(CH_3)_3$), 5.27 (dt, 1H, SiH, J = 11, 9, 9, and 9 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6) δ = −13.0 (dd, J(RhP) = 95 Hz, J(PP) = 32 Hz), −28.4 (dt, J(RhP) = 90 Hz, J(PP) = 32 Hz). Found: C, 48.87; H, 6.49%. Calcd for $C_{30}H_{44}OF_6P_3SSiRh{\cdot}C_6H_{14}$: C, 49.30; H, 6.67%.

3d: (obtained in a hexane-solvated form): Yield 36%; IR (KBr) 2048 (ν(SiH)), 1964 cm^{-1} (ν(RhH)); ^{1}H NMR (C_6D_6) δ = −9.15 (ddt, 1H, RhH, J = 153, 18, 18, and 16 Hz), 0.89 (d, 9H, $P(CH_3)_3$, J = 7 Hz), 1.07 (apparent triplet due to virtual coupling, 18H, $P(CH_3)_3$), 5.28 (quartet, 1H, SiH, J = 10 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6) δ = −13.0 (dd, J(RhP) = 95 Hz, J(PP) = 32 Hz), −28.4 (dt, J(RhP) = 90 Hz, J(PP) = 32 Hz). Found: C, 48.16; H, 6.62%. Calcd for $C_{30}H_{44}F_6P_3SSiRh{\cdot}0.5C_6H_{14}$: C, 48.47; H, 6.29%.

Thermal Reaction of Arenethiolato(diarylsilyl)hydridorhodium(III) Complexes. A typical example is as follows. A hexane (10 cm^3) dispersion of **1a** (60 mg, 0.096 mmol) was heated at 50 °C for 3 h. The complex was dissolved almost completely, accompanied by a solution color change to yellow. After a small amount of the remaining **1a** was removed by filtration, the solution was cooled at room temperature for 24 h and then at −20 °C for 12 h, resulting in the formation of pale orange crystals. The crystals were collected by filtration to give **4a** (24 mg, 40%). IR (KBr) 1930 and 1920 cm^{-1} (ν(RhH)); ^{1}H NMR (C_6D_6) δ = −10.05 (m, 2H, RhH, J(PH) = 117 Hz), 1.05 (d, 27H, $P(CH_3)_3$, J = 7 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6) δ = −18.4 (dd, J(RhP) = 101 Hz, J(PP) = 23 Hz), −24.1 (dt, J(RhP) = 90 Hz, J(PP) = 23 Hz). Found: C, 51.57; H, 6.52; S, 5.40%. Calcd for $C_{27}H_{44}SiP_3SRh$: C, 51.92; H, 7.10; S, 5.13%.

Thermal reaction of **2a** and **3a** was carried out similarly to lead to isolation of **5a** and **6a**, respectively.

5a: (38%): IR (KBr) 1949 and 1918 (ν(RhH)), 1239 cm^{-1} (ν(CO)); ^{1}H NMR (C_6D_6) δ = −10.02 (m, 2H, RhH, J(PH) = 117 Hz), 1.07 (d, 27H, $P(CH_3)_3$, J = 7 Hz), 3.15 (s, 3H, $C_6H_4OCH_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ = −18.3 (dd, J(RhP) = 100 Hz, J(PP) = 23 Hz), −24.1 (dt, J(RhP) = 90 Hz, J(PP) = 23 Hz). Found: C, 51.81; H, 7.63; S, 4.29%. Calcd for $C_{28}H_{46}OSiP_3SRh$: C, 51.80; H, 7.08; S, 4.90%.

6a: (34%): IR (KBr) 1962 and 1917 cm^{-1} (ν(RhH)); ^{1}H NMR (C_6D_6) δ = −10.02 (m, 2H, RhH, J(PH) = 117 Hz), 1.06 (d, 27H, $P(CH_3)_3$, J = 7 Hz), 1.94 (s, 3H, $C_6H_4CH_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ = −18.3 (dd, J(RhP) = 100 Hz, J(PP) = 23 Hz), −24.1 (dt, J(RhP) = 91 Hz, J(PP) = 23 Hz). Found: C, 52.75; H, 7.62; S, 4.72%. Calcd for $C_{28}H_{46}SiP_3SRh$: C, 52.66; H, 7.26; S, 5.02%.

Thermal reaction of **1b**, **2b**, **2c**, **2d**, **3c**, and **3d** and their kinetic studies were carried out in an NMR tube. Isolation of the respective products: **4b**, **5b**, **5c**, **5d**, **6c**, and **6d** were not examined, but the products are of high purity (> 97%).

4b: ^{1}H NMR (C_6D_6) δ = −9.97 (m, 2H, RhH, J(PH) = 117 Hz), 1.07 (d, 27H, $P(CH_3)_3$, J = 7 Hz), 2.18 (s, 6H, $C_6H_4CH_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ = −18.3 (dd, J(RhP) = 100 Hz, J(PP) = 23 Hz), −24.3 (dt, J(RhP) = 88 Hz, J(PP) = 23 Hz).

5b: IR (KBr) 1974 (ν(RhH)), 1230 cm^{-1} (ν(CO)); ^{1}H NMR (C_6D_6) δ = −9.98 (m, 2H, RhH, J(PH) = 117 Hz), 1.10 (d, 27H, $P(CH_3)_3$, J = 7 Hz), 2.20 (s, 6H, $C_6H_4CH_3$), 3.15 (s, 3H, $C_6H_4OCH_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ = −18.3 (dd, J(RhP) = 102 Hz, J(PP) = 23 Hz), −24.3 (dt, J(RhP) = 90 Hz, J(PP) = 23 Hz).

5c: ^{1}H NMR (C_6D_6) δ = −10.17 (m, 2H, RhH, J(PH) = 117 Hz), 1.04 (d, 27H, $P(CH_3)_3$, J = 5 Hz), 3.16 (s, 3H, $C_6H_4CH_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ = −18.5 (dd, J(RhP) = 101 Hz, J(PP) = 24 Hz), −24.2 (dt, J(RhP) = 90 Hz, J(PP) = 24 Hz).

5d: ^{1}H NMR (C_6D_6) δ = −10.27 (m, 2H, RhH, J(PH) = 116 Hz), 0.95 (d, 9H, $P(CH_3)_3$, J = 5 Hz), 1.00 (br, 18H), 3.16 (s, 3H, $C_6H_4CH_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ = −18.5 (dd, J(RhP) = 101 Hz, J(PP) = 24 Hz), −24.2 (dt, J(RhP) = 90 Hz, J(PP) = 24 Hz).

6c: ^{1}H NMR (C_6D_6) δ = −10.18 (m, 2H, RhH, J(PH) = 117 Hz), 1.03 (d, 27H, $P(CH_3)_3$, J = 7 Hz), 1.95 (s, 3H, $C_6H_4CH_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ = −18.5 (dd, J(RhP) = 100 Hz, J(PP) = 23 Hz), −24.2 (dt, J(RhP) = 91 Hz, J(PP) = 23 Hz).

6d: ^{1}H NMR (C_6D_6) δ = −10.33 (m, 2H, RhH, J(PH) = 117 Hz), 1.00 (d, 27H, $P(CH_3)_3$, J = 5 Hz), 1.94 (s, 3H, $C_6H_4CH_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ = −19.0 (dd, J(RhP) = 99 Hz, J(PP) = 23 Hz), −23.5 (dt, J(RhP) = 90 Hz, J(PP) = 23 Hz).

Kinetic Study. An NMR tube containing a benzene-d_6 solution of **3a** was connected to a vacuum line. After three cycles of pump and thaw, the top of the sample tube was sealed in a flame. The sample was allowed to warm in a thermostatted NMR probe. The reaction was followed by change in the peak intensity of the OMe hydrogens of the starting complex by using dioxane as the internal standard. Other kinetic measurements were performed similarly.

Crystal Structure Determination. Colorless crystals of **4a** (form I) suitable for crystallography were obtained together with pale yellow crystals of form II by recrystallization from acetone. These crystals were mounted in glass capillary tubes under argon. The unit cell parameters were obtained by least-squares refinement of 2θ values of 25 reflections with $20° \leq 2\theta < 30°$. Intensities were collected for Lorentz and polarization effects on a Rigaku AFC-5R automated four-cycle diffractometer by using Mo $K\alpha$ radiation (λ = 0.71069 Å) and ω–2θ scan method, and an empirical absorption correction (Ψ scan) was applied. Crystal data: $C_{27}H_{44}P_3SSiRh$; M_r, 624.62; triclinic; space group, $P\bar{1}$ (No. 2); a = 11.004(2), b = 14.449(2), c = 10.041(1) Å, α = 94.24(1)°, β = 93.17(1)°, γ = 92.44(1)°, V = 1587.9(7) Å^3, Z = 2, μ (Mo $K\alpha$) = 7.91 cm^{-1}, $F(000)$ = 652, D_{calcd} = 1.307 g cm^{-3}, crystal size, 0.3×0.4×0.4 mm×mm×mm; Unique reflections ($2\theta \leq 55°$), 7264; Used reflections ($I \geq 3\sigma(I)$), 6669; No. of variables, 302; R (F_o), 0.040; R_w (F_o), 0.078.

Calculations were carried out by using a program package TEXSAN on a DEC Micro VAX-II computer. Atomic scattering factors were obtained from the literature.[21] A full matrix least-squares refinement was used for non-hydrogen atoms with anisotoropic thermal parameters. Position of a hydrido ligand was determined by the difference Fourier technique, and refined isotropically, while the other hydrido ligand was not located in the final D-map. The other hydrogens were located by assuming ideal positions (d (C–H) = 0.95 Å) and included in the structure calculation without further refinement of the parameters. The crystallographic results including $F_o - F_c$ table are deposited as Document No. 71066 at the Office of the Editor of Bull. Chem. Soc. Jpn. and deposited with the Cambridge Crystallographic Data Centre.

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