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Thermal Si−C Bond Cleavage of LRhH(SiAr$_3$)(μ-H)(μ-Cl)RhH(SiAr$_3$)L (Ar = C$_6$H$_5$, C$_6$H$_4$F-*p*; L = P(*i*-Pr)$_3$) To Give LRhH(μ-SiAr$_3$)(μ-SiAr$_2$)(μ-Cl)RhHL Containing Symmetrically Bridging Triarylsilyl and Diarylsilylene Ligands

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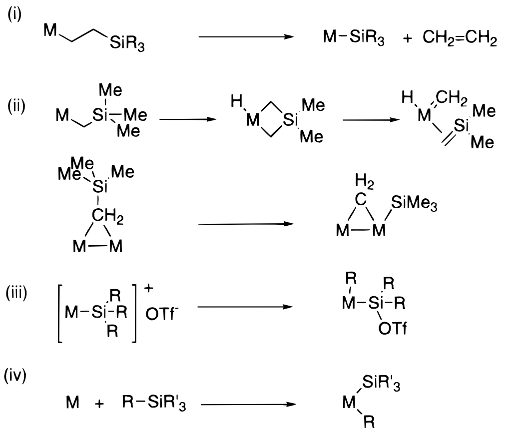
The reaction of dinuclear rhodium complex LRhH(SiPh$_3$)(μ-H)(μ-Cl)RhH(SiPh$_3$)L (**1**; L = P(*i*-Pr)$_3$) with excess HSi(C$_6$H$_4$F-*p*)$_3$ leads to replacement of the SiPh$_3$ ligands with the Si(C$_6$H$_4$F-*p*)$_3$ group to give LRhH[Si(C$_6$H$_4$F-*p*)$_3$](μ-H)(μ-Cl)RhH[Si(C$_6$H$_4$F-*p*)$_3$]L (**2**) at room temperature. HSiPh$_2$(C$_6$H$_4$F-*p*) and HSiPh(C$_6$H$_4$F-*p*)$_2$ also react with **1** to give LRhH[SiPh$_2$(C$_6$H$_4$F-*p*)](μ-H)(μ-Cl)RhH[SiPh$_2$(C$_6$H$_4$F-*p*)]L (**3**) and LRhH[SiPh(C$_6$H$_4$F-*p*)$_2$](μ-H)(μ-Cl)RhH[SiPh(C$_6$H$_4$F-*p*)$_2$]L (**4**), respectively. Heating of benzene or toluene solution of **1** and **2** at 60 °C results in Si−C bond cleavage of a triarylsilyl ligand and affords LRhH(μ-SiAr$_3$)(μ-SiAr$_2$)(μ-Cl)RhHL (**7**, Ar = Ph; **8**, Ar = C$_6$H$_4$F-*p*) accompanied by liberation of benzene and fluorobenzene, respectively. The NMR (^{1}H and ^{31}P) spectra of **7** and **8** indicate symmetrical coordination of the bridging triarylsilyl and diarylsilylene groups to two Rh centers. The reaction of **1** to form **7** at 55−70 °C obeys first-order kinetics with the kinetic parameters: $\Delta G^{\ddagger} = 112$ kJ mol^{-1}, $\Delta H^{\ddagger} = 129$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 58$ J mol^{-1} deg^{-1} at 298 K. Complexes **2**−**4** also undergo thermal Si−C bond cleavage of a triarylsilyl ligand to liberate fluorobenzene as the organic product. The rate constants of the reaction increase in the order **2** < **4** < **3** < **1**.

Introduction

Late transition metal complexes often cleave Si−C bonds of organosilicon compounds or Si-containing organic ligands under mild conditions. Scheme 1 summarizes several reaction patterns previously reported. Complexes of Fe and Ru with 2-silylethyl ligand undergo β-silyl group elimination to form a new metal−Si bond (i).[1] The reaction is involved in the transition-metal-catalyzed transsilylation of vinylsilane and related reactions as the crucial step.[2] A mononuclear Pt complex[3] and a dinuclear Ru complex[4] containing a trimethylsilylmethyl ligand undergo scission of Si−Me or CH$_2$−Si bond to give methylene-group-coordinated metal complexes (ii). A (triorganosilyl)iridium(III) complex was reported to yield a thermal reaction product containing a triflate-substituted diorganosilyl ligand. The reaction most probably proceeds through α-elimination of the organic group to give a silylene-coordinated intermediate followed by its reaction with a triflate counterion to form a Si−OTf bond (iii).[5] The oxidative addition of an unstrained or strained C−Si bond to low-valent Rh and Ru complexes was studied in detail (iv).[6] Synthetic organic reactions involving similar oxidative addition of the Si−C bond to a Cu or a Pd complex were recently reported.[7]

Scheme 1



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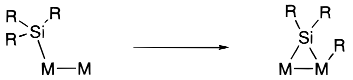
Scheme 2

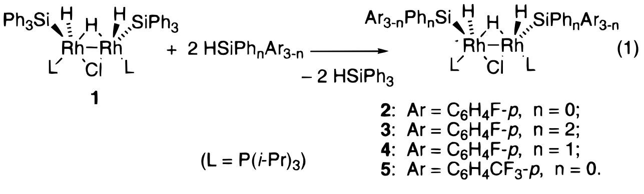


Dinuclear complexes of Pt, Ru, and Rh, which contain a nonbridging silyl ligand, provide another kind of Si−C bond activation. Scheme 2 depicts the oxidative addition of an Si−C bond in a triorganosilyl group bonded to one metal to the other metal center to afford a complex with a bridging diorganosilylene ligand. Such reactions in bimetallic systems occur smoothly, probably because of the high stability of the bridging coordination of the silylene group of the product as well as of the Si−C bond to be activated and the metal center, which are close to each other.[8b,9]

In this paper, we report the thermally induced Si−C bond cleavage of LRhH(SiAr$_3$)(μ-H)(μ-Cl)RhH(SiAr$_3$)L type complexes to afford new dinuclear Rh complexes with bridging triarylsilyl and diarylsilylene ligands. Part of this work has been reported in a preliminary form.[10]

Results

Exchange Reaction of LRhH(SiPh$_3$)(μ-H)(μ-Cl)-RhH(SiPh$_3$)L (1) with Triarylsilane at Room Temperature. LRhH(SiPh$_3$)(μ-H)(μ-Cl)RhH(SiPh$_3$)L (**1**, L = P(i-Pr)$_3$)[11] reacts with HSi(C$_6$H$_4$F-p)$_3$ in a 1:10 molar ratio at room temperature to give LRhH[Si(C$_6$H$_4$F-p)$_3$]-(μ-H)(μ-Cl)RhH[Si(C$_6$H$_4$F-p)$_3$]L (**2**) in 78% yield, as shown in eq 1. The molecular geometries of **1** and **2** are shown in Figures 1 and 2, respectively. Two Rh centers having triarylsilyl and P(i-Pr)$_3$ ligands are bridged by hydrido and chloro ligands, similarly to the previously reported X-ray structure of LRhH[Si(C$_6$H$_4$OCF$_3$-p)$_3$](μ-H)(μ-Cl)RhH[Si(C$_6$H$_4$OCF$_3$-p)$_3$]L. The Rh−Rh distances (2.810(2) and 2.815(1) Å) are in the range of that previously reported for dinuclear organorhodium complexes with the Rh−Rh bond.[8c,9 g−j,12] Two nonbridging hydrido ligands of **1** and **2** are situated at anti positions of the Rh−Cl−Rh−H1(bridging) four-membered ring



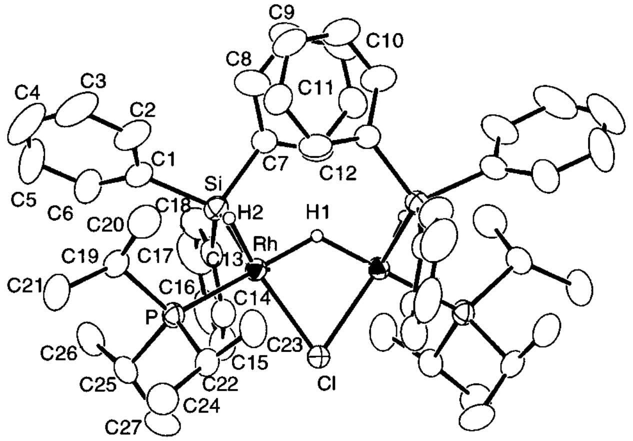


Figure 1. Perspective drawing of complex **1**. The molecule has a crystallographic C_2 symmetry around the midpoint of the Rh−Rh bond. Selected bond distances (Å) and angles (deg): Rh−Rh, 2.815(1); Rh−Cl, 2.413(2); Rh−P, 2.314(2); Rh−Si, 2.289(2); Rh−H(1), 1.59(2); Rh−H(2), 1.37(5); Rh−Rh−Cl, 54.32(4); Rh−Rh−P, 150.97(6); Rh−Rh−Si, 101.74(6); Rh−Rh−H(1), 27.(1); Rh−Rh−H(2), 119.(1); Cl−Rh−P, 98.98(7); Cl−Rh−Si, 127.97(6); Cl−Rh−H(1), 81.(1); Cl−Rh−H(2), 165.(2); P−Rh−Si, 104.58(8); P−Rh−H(1), 167.6(2); P−Rh−H(2), 82.(1); Si−Rh−H(1), 84.(1); Si−Rh−H(2), 65.(2); H(1)−Rh−H(2), 93.(2); Rh−Cl−Rh, 71.37(8); Rh−H(1)−Rh, 126.

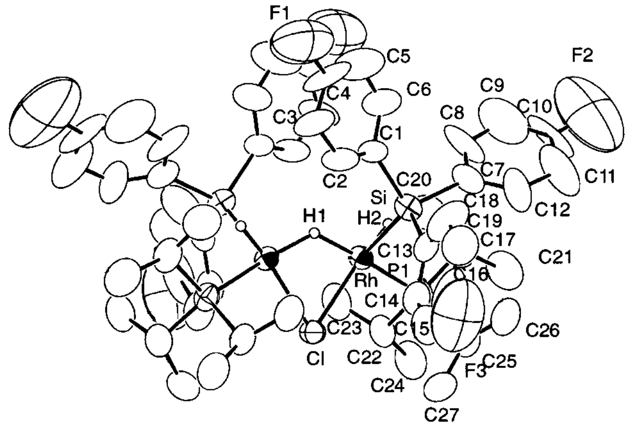


Figure 2. Perspective drawing of complex **2**. The molecule has a crystallographic C_2 symmetry around the midpoint of the Rh−Rh bond. Selected bond distances (Å) and angles (deg): Rh−Rh, 2.810(2); Rh−Cl, 2.415(4); Rh−P, 2.309(4); Rh−Si, 2.293(4); Rh−H(1), 1.55; Rh−H(2), 1.30; Rh−Rh−Cl, 54.42(8); Rh−Rh−P, 151.6(1); Rh−Rh−Si, 101.0(1); Rh−Rh−H(1), 25; Rh−Rh−H(2), 136; Cl−Rh−P, 98.5(1); Cl−Rh−Si, 127.2(1); Cl−Rh−H(1), 80; Cl−Rh−H(2), 164; P−Rh−Si, 104.7(2); P− Rh−H(1), 168; P−Rh−H(2), 67; Si−Rh−H(1), 85; Si−Rh−H(2), 67; H(1)−Rh-H(2), 111; Rh−Cl−Rh, 71.2(1); Rh−H(1)−Rh, 130.

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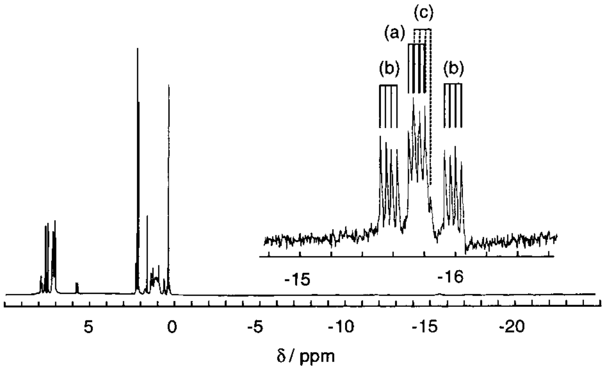
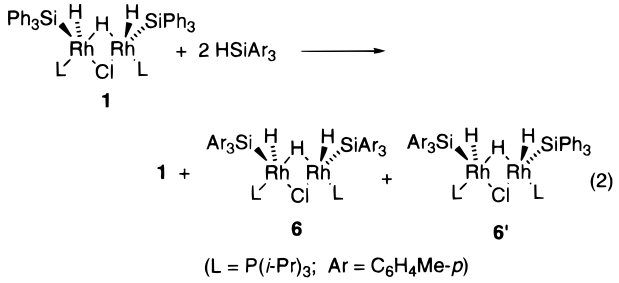


Figure 3. ^1H NMR spectrum of the reaction product of $HSi(C_6H_4Me\text{-}p)_3$. The signals in the range of δ −15.5 to −16.1 are assigned to nonbridging hydrido ligands of (a) **1**, (b) **6′**, and (c) **6**.

plane in order to reduce steric repulsion between the triarylsilyl ligands. The NMR (^1H and ^{31}P) spectra of **2** are similar to those of **1** and are consistent with the crystal structure.

Triarylsilanes with electron-withdrawing substituents, $HSiPh_2(C_6H_4F\text{-}p)$, $HSiPh(C_6H_4F\text{-}p)_2$, and $HSi(C_6H_4CF_3\text{-}p)_3$, also react with **1** at room temperature to give dinuclear complexes $LRhH[SiPh_2(C_6H_4F\text{-}p)](\mu\text{-}H)(\mu\text{-}Cl)RhH[SiPh_2(C_6H_4F\text{-}p)]L$ (**3**), $LRhH[SiPh(C_6H_4F\text{-}p)_2](\mu\text{-}H)(\mu\text{-}Cl)RhH[SiPh(C_6H_4F\text{-}p)_2]L$ (**4**), and $LRhH[Si(C_6H_4CF_3\text{-}p)_3](\mu\text{-}H)(\mu\text{-}Cl)RhH[Si(C_6H_4CF_3\text{-}p)_3]L$ (**5**), respectively. Complexes **3** and **4** were isolated and characterized by NMR spectroscopy, and their spectra are similar to those of **1** and **2**, while complex **5** was characterized in situ by NMR spectroscopy without isolation.

The reaction of $HSi(C_6H_4Me\text{-}p)_3$ with **1** in a 4:1 molar ratio leads to the formation of a mixture of $LRhH[Si(C_6H_4Me\text{-}p)_3](\mu\text{-}H)(\mu\text{-}Cl)RhH[Si(C_6H_4Me\text{-}p)_3]L$ (**6**), $LRhH[Si(C_6H_4Me\text{-}p)_3](\mu\text{-}H)(\mu\text{-}Cl)RhH(SiPh_3)L$ (**6′**), and unreacted **1** in a molar ratio of 44:12:44 (eq 2). Figure 3 depicts the ^1H NMR spectrum of the mixture. The four signals in the range of δ −15.5 to −16.1 are assigned to the nonbridging hydrido ligands of the complexes. The signal at δ −15.78 due to **1** overlaps with that due to **6** (δ −15.81), whereas two signals at δ −15.59 and −16.01 with equal intensity are assigned to the two nonbridging hydrido ligands of **6′** having an unsymmetrical structure. Similar reaction in a 10:1 molar ratio leads to formation of not only **1**, **6**, and **6′** (6:68:26) but also a new complex (ca. 25% of the product) formed through further reaction of **6** and **6′** under the reaction conditions.



(2)

(L = P(*i*-Pr)$_3$; Ar = $C_6H_4Me\text{-}p$)

Complex **1** was prepared by reacting $HSiPh_3$ with $RhClL_2$ to form $RhCl(H)(SiPh_3)L_2$ initially, which was followed by its further reaction with $HSiPh_3$.[11] Attempts to obtain **2** and **6** by a similar reaction of the triarylsilane with $RhClL_2$ were unsuccessful owing to the low reactivity of $HSiAr_3$ (Ar = $C_6H_4Me\text{-}p$, $C_6H_4F\text{-}p$) with initially formed mononuclear $RhCl(H)(SiAr_3)L_2$.

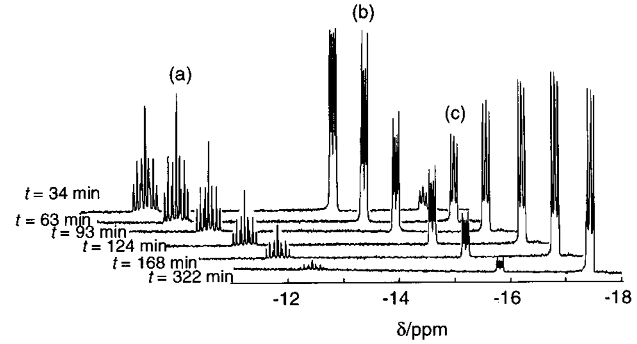
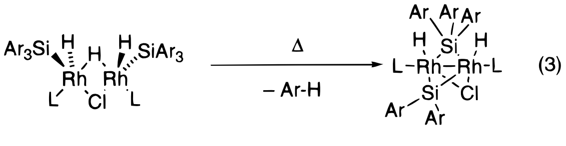


Figure 4. Changes in the ^1H NMR spectra (hydrido region) during thermal reaction of **1** to give **7** at 70 °C. Signals a and b are assigned to bridging and nonbridging hydrido ligands of **1**, while signal c is assigned to the hydrido ligands of **7**.

Thermal Si−C Bond Cleavage Reaction of 1 and 2. Heating of a benzene or toluene solution of **1** and **2** at 60 °C leads to the conversion of the complexes to $LRhH(\mu\text{-}SiAr_3)(\mu\text{-}SiAr_2)(\mu\text{-}Cl)RhHL$ (**7**, Ar = Ph; **8**, Ar = $C_6H_4F\text{-}p$), as shown in eq 3. Gas chromatographic analyses of the product showed quantitative formation of benzene and fluorobenzene, respectively. The X-ray structure of **8**, having symmetrical coordination of the triarylsilyl and diarylsilylene ligands, was shown in our preliminary report.[10] The ^1H NMR spectra of **7** and **8** exhibit signals due to two equivalent hydrido ligands at δ −17.40 and −17.60, respectively. The splitting pattern assigned to the AA′ part of an AA′MM′XX′ pattern indicates nonbridging coordination of the hydrido ligand. In agreement with the presence of two unequivalent Si centers bridging to two Rh centers, the $^{29}Si\{^1H\}$ NMR spectrum of **7** contains signals at δ 157.8 and 28.7. The former signal appears as a triplet of triplets, while the latter is observed as a triplet. The former signal may be assigned to the Si of the $SiPh_2$ ligand because the ^{29}Si NMR signal of most bridging diorganosilylene ligands bonded to two transition metal centers was observed at lower magnetic field positions than δ 80.[8b,9k,n,13]



(3)

1: Ar = C_6H_5
2: Ar = $C_6H_4F\text{-}p$

7: Ar = C_6H_5
8: Ar = $C_6H_4F\text{-}p$

The ^1H and $^{31}P\{^1H\}$ NMR spectra obtained during the reaction contain signals of the above starting complexes and the product only. Figure 4 shows a decrease in the ^1H NMR signal intensity of the hydrido of **1** and an increase in that of **7** during the reaction at 70 °C. The first-order plots of the reaction obtained from peak

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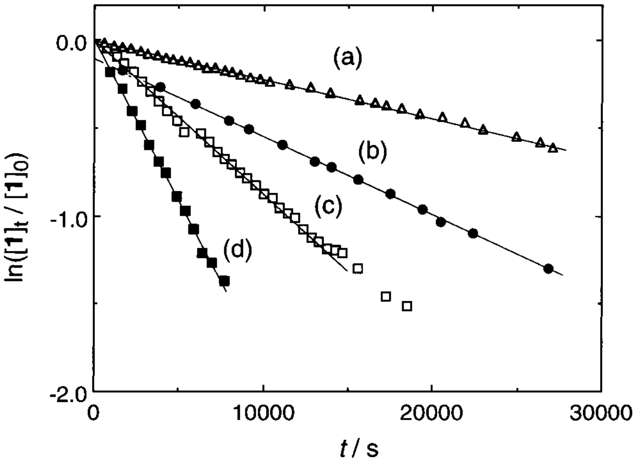

Figure 5. First-order plots of reaction of **1** to **7** obtained from changes in ^{1}H NMR peak intensity of the hydrido ligand of **1** at (a) 328, (b) 333, (c) 338, and (d) 343 K.

Table 1. Kinetic Results of Thermal Reaction of LRhH(SiAr$_3$)(μ-H)(μ-Cl)RhH(SiAr$_3$)L and LRhH(SiArAr′$_2$)(μ-H)(μ-Cl)RhH(SiAr$_2$Ar′)L

complex				
	Ar	Ar′	temp/K	k/s^{-1}
1	C_6H_5	–	328	2.16×10^{-5}
		–	333	4.41×10^{-5}
		–	338	8.51×10^{-5}
		–	343	1.82×10^{-4}
2	C_6H_4F-p	–	333	1.42×10^{-5}
3	C_6H_4F-p	C_6H_5	333	3.01×10^{-5}
4	C_6H_5	C_6H_4F-p	333	1.96×10^{-5}

intensity relative to an internal standard are linear at 55−70 °C and indicate the first-order kinetics with respect to [**1**], as shown in Figure 5. Table 1 summarizes the rate constants. The kinetic parameters were obtained from the temperature dependence of the rate constants as $\Delta G^{\ddagger} = 112$ kJ mol^{-1}, $\Delta H^{\ddagger} = 129$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 58$ J mol^{-1} deg^{-1} at 298 K.

The thermal reaction of **3** and **4** gives fluorobenzene rather than benzene. The selective activation of an Si−C_6H_4F-p bond should afford LRhH[μ-SiPh$_2$(C$_6$H$_4$F-p)][μ-SiPh(C$_6$H$_4$F-p)](μ-Cl)RhHL and LRhH[μ-SiPh(C$_6$H$_4$F-p)$_2$][μ-SiPh(C$_6$H$_4$F-p)](μ-Cl)RhHL, respectively. The ^{1}H NMR spectrum of the product of the reaction of **4** shows the hydrido signal (δ − 17.60) whose complicated peak pattern indicates the presence of isomers caused by a difference in position of the Ph group in the bridging SiPh(C$_6$H$_4$F-p) and SiPh$_n$(C$_6$H$_4$F-p)$_{3-n}$ (n = 1,2) ligands. The rate constants of the reaction increase in the order **2** < **4** < **3** < **1** as shown in Table 1, suggesting that the introduction of fluorine at the para position of the triarylsilyl ligand retards the Si−C bond cleavage reaction.

Discussion

The dinuclear Rh complexes LRhH(SiAr$_3$)(μ-H)(μ-Cl)RhH(SiAr$_3$)L undergo exchange of the triarylsilyl ligand on addition of another triarylsilane and thermal Si−C bond activation of an SiAr$_3$ ligand to form a product with bridging triarylsilyl and diarylsilylene ligands. The exchange of the organosilyl ligand was also reported to occur in several other mononuclear and dinuclear transition metal complexes containing a M−Si bond. Dinuclear Fe and Ru complexes with bridging methylene and carbonyl ligands and a terminal triorganosilyl ligand undergo smooth silyl ligand exchange on addition of triorganosilane.[13d,14] Our previous study on the reaction of diarylsilane with *mer*-RhCl(H)(SiHAr$_2$)(PMe$_3$)$_3$ established the facile exchange of the diarylsilyl ligand through reductive elimination of diarylsilane from the complex followed by its oxidative addition.[15] Measurement of the equilibrium constants revealed the relative stability of the Rh−Si bond in the order Rh−SiH(C$_6$H$_4$F-p)$_2$ > Rh−SiHPh$_2$ > Rh−SiH(C$_6$H$_4$Me-p)$_2$. Reactions in eq 1 turn the SiPh$_3$ ligand of **1** into the fluorinated triarylsilyl ligand of the product, whereas exchange of the SiPh$_3$ ligand of **1** on addition of HSi(C$_6$H$_4$Me-p)$_3$ gives **6** and **6′** together with unreacted **1**. These results seem to suggest a lower thermodynamic stability of the Rh−Si(C$_6$H$_4$Me-p)$_3$ bond than the Rh−Si(C$_6$H$_4$F-p)$_3$ bond of the present dinuclear complexes.

The bridging coordination of a triorganosilyl group to Na, Al, and B to form the M−Si−M bond is regarded as an analogue of the M−H−M three-center, two-electron bond of nontransition metals.[16] Most of the silyl ligand bridged dinuclear transition metal complexes contain an SiHR$_2$ ligand that is bonded to one metal through a σ-bond and to another metal through the Si−H−M three-center, two-electron bond, as shown in Chart. Such μ-η^1,η^2-coordination of the ligand renders the distances between the two M−Si bonds different.[9,17] There have been only a few reports on transition metal complexes with bridging triorganosilyl ligands. A dinuclear platinum complex with bridging SiMeCl$_2$ ligand was reported although no crystallographic study was done.[18] Dinuclear or tetranuclear copper complexes with a sterically demanding Si(SiMe$_3$)$_3$ group as the bridging ligands were characterized structurally.[19] A diplatinum complex with symmetrically bridging triorganophosphine that is isolobal to the triorganosilyl anion was reported by Braunstein and co-workers.[20]

Complex **8** obtained in this study showed unique structural properties as follows. The distances between Rh centers and the Si atom of the triarylsilyl ligand are similar (2.444(4) and 2.487(3) Å) and are significantly longer than the bonds between Si of the silylene ligand and Rh centers (2.290(3) and 2.250(3) Å) as well as the Rh−Si σ-bond distances already reported (2.203-2.379 Å). They are comparable even to the Rh−Si distance in a Rh−H−Si three-center, two-electron bond (2.487 Å). This contrasts with the previous observation that the Cu complexes containing Si(SiMe$_3$)$_3$ ligands showed no significant differences in the distances between the bridging and nonbridging Cu−Si bonds.

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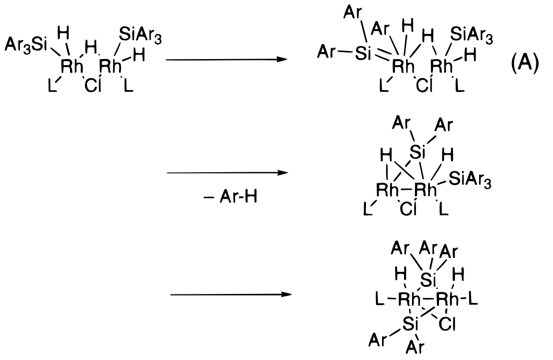
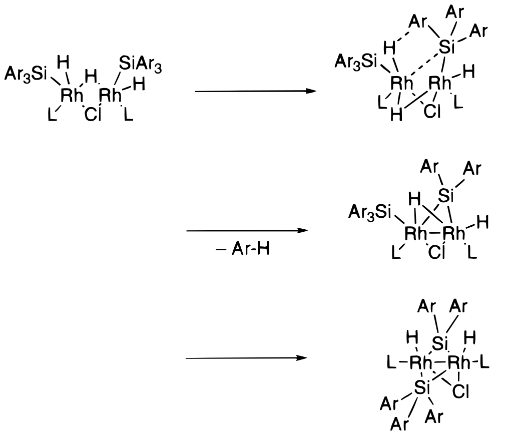
Scheme 3



Scheme 4



Several pathways are conceivable for the thermal reaction of **1** and **2** to give **7** and **8**, respecitvely. Scheme 3 shows a pathway involving α-elimination of an aryl group of the triarylsilyl ligand of the starting complex followed by reductive elimination of arene and a change in coordination of the diarylsilylene group to a more stable bridging one. The reaction of **3** and **4** leading to selective formation of fluorobenzene and the rate constants in the order **2** < **4** < **3** < **1** can be rationalized by assuming that the reaction involves formation of an intermeidate (A) as the rate determining step. Fluoro substituents of the produced diarylsilylene ligand destabilize the intermediate and retard the reaction, while the $Si-C_6H_4F$-*p* bond is cleaved more readily than the Si–Ph bond to leave a smaller number of fluorine substituents in the diarylsilylene ligand. On the other hand, products with diarylsilyl ($SiHAr_2$) or chlorodiarylsilyl ($SiClAr_2$) ligands, which may be expected from the chloro(hydrido)rhodium intermediate having a Rh═Si double bond, were not formed at all.

Scheme 4 depicts a plausible reaction pathway involving an intramolecular σ-bond metathesis type reaction of a Si–Ar bond with a Rh–H bond. The direct elimination of Ar–H followed by a change in the coordination mode of a hydrido and a triarylsilyl ligand between bridging and nonbridging will lead to the product. The positive activation entropy of the reaction is consistent with the mechanism. The elimination of fluorobenzene from the reaction of **3** and **4** can be attributed to the relief of the mismatching of polarization of the $Si^{\delta+}-C^{\delta-}$ and $Rh^{\delta+}-H^{\delta-}$ bonds in the initial reaction caused by the electron-withdrawing fluorine substituent. The fluorine substituent serves also to stabilize the Rh–Si bond of the starting complex and to retard the initial reaction involving activation of the Rh–Si bond of nonbridging triarylsilyl ligand turning it into a semibridging one. The pathway contains a smaller number of reaction steps than the other and does not require sterically congested intermediate complexes. Although the σ-bond metathesis reaction was uncommon in electron rich late transition metal complexes with phosphine ligands, such a sterically rigid system with close Rh–H and Si–aryl bonds may enable the electronically disfavored bond activation involving the four-center transition state.

The pathways in Schemes 3 and 4 seem to be more favored than the others, while it is not feasible to decide which of the mechanisms is operative for the Si–C bond cleavage reaction.[21] Other reactions involving Rh–Rh bond splitting or a shift of the bridging chloro ligand to a terminal position may also trigger the Si–C bond cleavage.

Recently, the triorganosilyl ligand transfer from one metal to the other in a dinuclear metal system was found by Braunstein, Girolami, Akita, and their respective co-workers.[3,22] These reactions should involve a triorganosilyl group bridging a dinuclear complex as the transition-state species or the unstable intermediate since these reactions proceed very rapidly under mild conditions. The present study has provided the dinuclear Rh complexes with bridging triarylsilyl ligands. The complexes have high thermal stability despite the significantly longer Rh–Si bond than the common Rh–Si single bond observed in the crystal structure. The formation of the complexes involves a change in the coordination of a nonbridging triarylsilyl ligand to a bridging one, which corresponds to the process of converting the nonbridging triorganosilyl ligand in the dinuclear complexes to a high-energy species during the above triorganosilyl ligand transfer reaction.

Experimental Section

General Considerations, Measurement, and Materials. Manipulation of Rh complexes was carried out under nitrogen or argon using standard Schlenk techniques. $RhClL_2$, **1**, and triarylsilanes were prepared according to the literature.[23] $HSiPh(C_6H_4F$-*p*$)_2$ and $HSiPh_2(C_6H_4F$-*p*$)$ were prepared from reactions of FC_6H_4MgBr with $HSiPhCl_2$ and with $HSiPh_2Cl$, respectively. NMR spectra (^1H and ^{31}P) were recorded on a JEOL EX-400 spectrometer. $^{31}P\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4 and to external $SiMe_4$, respectively. Elemental analyses were carried out by

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[21] Rate constants of the thermal reaction of **1** are increased significantly by addition of $HSiPh_3$ (60 °C, $[\mathbf{1}]_0 = 0.053$ mM in benzene); 10^5k (s^{-1}) = 4.41 ($[HSiPh_3] = 0$), 7.32 ($[HSiPh_3]/[\mathbf{1}] = 1.02$), 13.2 ($[HSiPh_3]/[\mathbf{1}] = 2.00$), and 11.5 ($[HSiPh_3]/[\mathbf{1}] = 4.00$). There seem to be two possible rationales for the remarkable influence of the additive. Added $HSiPh_3$ may shift an equilibrium of reductive elimination of $HSiPh_3$ and its reoxidative addition to regenerate **1** and serve to increase the concentration of **1** in the equilibrated mixture. Alternatively, the Si–C bond cleavage reaction involving a different mechanism from that without addition of $HSiPh_3$ may occur in the presence of added $HSiPh_3$. The observations do not seem to provide any clue to elucidate the mechanism.

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a Yanaco MT-5 CHN autocorder. Gas chromatographic measurement was carried out on a Shimadzu GC-8A equipped with a 2 m Silicone OV-1 packed column.

Preparation of 2−5. To a toluene (5 mL) solution of **1** (41 mg, 0.038 mmol) was added $HSi(C_6H_4F\text{-}p)_3$ (120 mg, 0.38 mmol) at room temperature. After stirring for 2 h at that temperature, the solvent was reduced to ca. 2 mL under vaccum. Removal of a small amount of insoluble solid followed by addition of pentane to the filtrate resulted in separation of **2** as yellow crystals (35 mg, 78%). ^1H NMR: δ 7.59 (dd, 12H, *ortho*, $J(HH) = 6$ Hz, $J(HF) = 7$ Hz), 6.90 (dd, 12H, *meta*, $J(HH) = 6$ Hz, $J(HF) = 9$ Hz), 1.54 (m, 6H, P−CH, $J = 7$ Hz), 0.82 (br, 36H, CH_3), −12.55 (tt, 1H, Rh−H−Rh, $J(Rh-H) =$ 58 Hz, $J(P-H) = 25$ Hz), −16.07 (AA′ part of an AA′MM′XX′ pattern, 2H, Rh−H). $^{31}P\{^1H\}$ NMR: δ 54.2 (AA′ part of an AA′XX′ pattern). Anal. Calcd for $C_{54}H_{68}ClF_6P_2Rh_2Si_2$: C, 54.43; H, 5.84. Found: C, 53.98; H, 5.97.

Reactions of $HSiPh_2(C_6H_4F\text{-}p)$ and of $HSiPh(C_6H_4F\text{-}p)_2$ with **1** gave complexes $LRhH[SiPh_2(C_6H_4F\text{-}p)](\mu\text{-}H)(\mu\text{-}Cl)RhH[SiPh_2(C_6H_4F\text{-}p)]L$ (**3**) (68%) and $LRhH[SiPh(C_6H_4F\text{-}p)_2](\mu\text{-}H)(\mu\text{-}Cl)RhH[SiPh(C_6H_4F\text{-}p)_2]L$ (**4**) (28%), respectively. Data of **3** (obtained in a toluene solvated form). ^1H NMR (C_6D_6): δ 7.76 (d, 8H, *ortho* hydrogen of SiPh, $J = 6$ Hz), 7.74 (t, 4H, *ortho* hydrogen of $SiC_6H_4F\text{-}p$, $J(HH) = J(HF) = 8$ Hz), 7.13−7.23 (m, 12 H, *meta* and *para* hydrogen of SiPh), 6.87 (t, 4H, *meta* hydrogen of $SiC_6H_4F\text{-}p$, $J(HH) = J(HF) = 8$ Hz), 1.7 (br, 6H, P−CH), 0.7−1.0 (br, 36H, CH_3), −12.28 (tt, 1H, Rh−H−Rh, $J(Rh-H) = 58$ Hz, $J(P-H) = 25$ Hz), −15.83 (AA′ part of an AA′MM′XX′ pattern, 2H, Rh−H). $^{31}P\{^1H\}$ NMR: δ 53.6 (AA′ part of an AA′XX′ pattern). Anal. Calcd for $C_{54}H_{73}ClF_2P_2Rh_2Si_2 \cdot C_7H_8$: C, 60.47; H, 6.74. Found: C, 60.23; H, 6.36. Data of **4**: ^1H NMR (C_6D_6): δ 7.74 (d, 4H, *ortho* hydrogen of SiPh, $J = 6$ Hz), 7.67 (dd, 8H, *ortho* hydrogen of $SiC_6H_4F\text{-}p$, $J(HH) = J(HF) = 8$ Hz), 7.12−7.22 (m, 6 H, *meta* and *para* hydrogen of SiPh), 6.91 (t, 8H, *meta* hydrogen of $SiC_6H_4F\text{-}p$, $J(HH) = J(HF) = 8$ Hz), 1.6 (br, 6H, P−CH), 0.7−1.0 (br, 36H, CH3), −12.42 (tt, 1H, Rh−H−Rh, $J(Rh-H) = 59$ Hz, $J(P-H) = 23$ Hz), −15.98 (AA′ part of an AA′MM′XX′ pattern, 2H, Rh−H). $^{31}P\{^1H\}$ NMR: δ 53.9 (AA′ part of an AA′XX′ pattern). Anal. Calcd for $C_{54}H_{71}ClF_4P_2Rh_2Si_2$: C, 56.13; H, 6.19. Found: C, 55.68; H, 5.80.

Similar reaction of $HSi(C_6H_4CF_3\text{-}p)_3$ with **1** led to conversion of the Rh complex to $LRhH[Si(C_6H_4CF_3\text{-}p)_3](\mu\text{-}H)(\mu\text{-}Cl)RhH[Si(C_6H_4CF_3\text{-}p)_3]L$ (**5**), which showed NMR signals similar to **1** and **2**. Isolation of **5** as crystals was not feasible. Data of **5**: ^1H NMR (C_6D_6): δ 7.58 (d, 12H, *ortho*, $J = 7$ Hz), 7.47 (d, 12H, *meta*, $J = 7$ Hz), 1.42 (m, 6H, P−CH), 0.7 (br, 36H, CH_3), −12.69 (tt, 1H, Rh−H−Rh, $J(Rh-H) = 56$ Hz, $J(P-H) = 25$ Hz), −16.21 (AA′ part of an AA′MM′XX′ pattern, 2H, Rh−H). $^{31}P\{^1H\}$ NMR: δ 54.9 (AA′ part of an AA′XX′ pattern).

Reaction of 1 with $HSi(C_6H_4Me\text{-}p)_3$. To a toluene (1 mL) solution of **1** (91 mg, 0.084 mmol) was added $HSi(C_6H_4Me\text{-}p)_3$ (102 mg, 0.34 mmol). The solution was stirred for 24 h at room temperature. After removing the solvent under vacuum, the product was dissolved in C_6D_6 and was analyzed by ^1H NMR spectroscopy. The spectrum contains a mixture of **1**, **6**, and **6′** in a molar ratio of 44:12:44.

The product of similar reaction in a 1:10 molar ratio contained not only **1**, **6**, and **6′** but also a new complex that showed the ^1H hydrido signal at δ −17.25 and the $^{31}P\{^1H\}$ signal at δ 57.1. Positions and the coupling pattern of the signals are similar to those of **7** and **8**. Thus, the complex may be tentavely assigned to $LRhH[\mu\text{-}Si(C_6H_4Me\text{-}p)_2][\mu\text{-}Si(C_6H_4Me\text{-}p)_3](\mu\text{-}Cl)RhHL$ formed *via* the Si−C bond cleavage of **6** at room temperature. Isolation nor further characterization of the complex was infeasible.

Table 2. Crystal Data and Details of Structure Refinement of 1 and 2

compd	**1**	**2**
formula	$C_{54}H_{75}ClP_2Si_2Rh_2$	$C_{54}H_{69}ClF_6P_2Si_2Rh_2$
mol wt	1083.57	1191.51
cryst syst	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)
a (Å)	21.140(5)	21.400(9)
b (Å)	10.465(4)	10.678(4)
c (Å)	24.313(3)	24.277(10)
β (deg)	92.27(1)	93.49(3)
V (Å^3)	5374	5537
Z	4	4
μ (cm^{-1})	7.89	7.87
F(000)	2256	2448
D_{calcd} (g cm^{-3})	1.340	1.430
crystal size (mm × mm × mm)	0.3 × 0.4 × 0.4	0.3 × 0.5 × 0.5
2 θ range (deg)	5.0−50.0	5.0−55.0
measrd reflcns	4507	5339
unique reflcns	4355	5360
used reflcns ($I > 3\sigma(I)$)	2255	1804
no. of variables	282	303
R	0.042	0.061
R_w[a]	0.032	0.041
GOF	1.35	2.15

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

Preparation of 7 and 8. A toluene (5 mL) solution of **1** (264 mg, 0.24 mmol) was heated for 2 h at 70 °C. The color of the solution turned from yellow to orange during the reaction. GC analysis of the solution showed formation of benzene in a quantitative amount. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed peaks due to **7** only. Addition of pentane to the reaction mixture led to the separation of **7** as yellow orange crystals that were collected by filtration, washed with pentane, and dried in vacuo (71 mg, 29%). The low isolated yield is due to loss of the product during the isolation. ^1H NMR (C_6D_6, 400 MHz at 25 °C): δ 6.9−8.2 (m, 25H, aromatic), 1.18 (m, 6H, P−C*H*−CH$_3$, $J = 7.3$ Hz), 0.95 (qd, 18H, P−CH−C*H*$_3$, $J = 7.3$ Hz), −17.40 (AA′ part of an AA′MM′XX′ pattern, 2H, Rh−H). $^{31}P\{^1H\}$ NMR (C_6D_6, 160 MHz at 25 °C): δ 57.4 (AA′ part of an AA′XX′ pattern). $^{29}Si\{^1H\}$ NMR (C_6D_6, 80 MHz at 25 °C): δ 157.8 (t, $J = 50$ Hz), 28.7 (tt, $J = 50$ and 8 Hz). Anal. Calcd $C_{48}H_{69}ClP_2Rh_2Si_2$: C, 57.34; H, 6.92; Cl, 3.53. Found: C, 57.67; H, 7.01; Cl, 2.93.

Similar heating of a toluene solution of **2** gave **8** (51%). ^1H NMR: δ 6.76−7.88 (m, 20H, aromatic), 1.12 (m, 6H, P−C*H*−CH$_3$), 0.86 (qd, 18H, P−CH−C*H*$_3$) −17.60 (AA′ part of an AA′MM′XX′ pattern, 2H, Rh−H). $^{31}P\{^1H\}$ NMR (C_6D_6, 160 MHz at 25 °C): δ 58.2 (AA′ part of an AA′XX′ pattern). $^{29}Si\{^1H\}$ NMR (C_6D_6, 80 MHz at 25 °C): δ 155.2 (t, $J = 50$ Hz), 21.9 (tt, $J = 50$ and 8 Hz). Anal. Calcd for $C_{48}H_{64}ClF_5P_2Rh_2Si_2$: C, 52.63; H, 5.89. Found: C, 52.81; H, 5.89.

Kinetic Study. To an NMR tube containing **1** (23 mg) was introduced C_6D_6 (0.40 mL) by vacuum-transfer technique. Change of peak intensity of hydrido peaks was monitored relative to tetramethylsilane as internal standard by keeping the temperature of the NMR probe at 60 °C. Kinetic measurement of **1** at the other temperatures and of **2**−**4** were carried out analogously.

X-ray Crystallographic Study. The data were collected on a Rigaku AFC5R diffractometer at ambient temperature (23 °C) using the ω-scan mode. Correction for Lorentz and polarization effects, and an empirical absorption correction (Ψ-scan) were applied. Atomic scattering factors were taken from the literature.[24] The structure was solved by a combination of direct method and subsequent Fourier technique. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically. Hydrido ligands were located by difference Fourier technique and refined isotropically (**1**) or included in the calculation without further refinement (**2**). The other hydrogens were located by assuming ideal positions

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

(d(C−H) = 0.95 Å) and included in the structure calculation without further refinement of the parameters. Crystal data and results of structure refinement were summarized in Table 2.

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Supporting Information Available: Tables of crystallographic data of complexes **1** and **2** (12 pages). Ordering information is given on any current masthead page.

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