

Reactions of Diruthenium Tetrahydride Complex $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\mu\text{-H})_4\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)$ with Vinylsilanes: Formation of a μ -Silylene Complex via Successive Si–H and Si–C Bond Cleavage of Dimethylvinylsilane

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The diruthenium complex $\{\text{Cp}^*\text{Ru}(\mu\text{-H})\}_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HSiMe}_2(\text{CH}=\text{CH}_2)\}$ (**5a**; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) containing a μ -vinylsilane ligand was prepared by the reaction of $\text{Cp}^*\text{Ru}(\mu\text{-H})_4\text{RuCp}^*$ (**1**) with dimethylvinylsilane. The $\mu\text{-}\eta^2\text{:}\eta^2$ -coordination mode of dimethylvinylsilane was confirmed by means of ^1H , ^{13}C , and ^{29}Si NMR and IR spectroscopy. The Si–C(sp²) bond of **5a** was readily cleaved upon thermolysis with liberating hydrogen and resulted in formation of the μ -silylene, μ -ethylidyne complex $(\text{Cp}^*\text{Ru})_2(\mu\text{-SiMe}_2)(\mu\text{-CCH}_3)(\mu\text{-H})$ (**8**) via the μ -silyl, μ -vinyl complex $(\text{Cp}^*\text{Ru})_2(\mu\text{-}\eta^2\text{-HSiMe}_2)(\mu\text{-}\eta^2\text{-CH}=\text{CH}_2)$ (**9a**) as an intermediate. The reaction of **1** with trimethylvinylsilane rendered cleavage of both Si–C(sp²) and Si–C(sp³) bonds, which resulted in formation of **8**. Treatment of **8** with carbon monoxide led to formation of the μ -ethylidene complex by migration of the hydride to the bridging carbon; thus $\{\text{Cp}^*\text{Ru}(\text{CO})\}_2(\mu\text{-CHMe})(\mu\text{-SiMe}_2)$ (**10**) was obtained. The reaction of **8** with ethylene afforded the μ -vinyl, μ -silylene complex $(\text{Cp}^*\text{Ru})_2(\mu\text{-}\eta^2\text{-CH}=\text{CH}_2)(\mu\text{-SiMe}_2)(\mu\text{-H})(\text{CH}_2=\text{CH}_2)$ (**11**). The reaction of **8** with molecular hydrogen resulted in a re-formation of **1** with liberating dimethylethylsilane, which showed formation of the Si–C bond on the dinuclear system. The molecular structures of **5a**, **8**, and **10** were determined by single-crystal X-ray diffraction studies.

Introduction

Activation of an inert bond, such as C–H and C–C bonds, has been an attractive and challenging target of organometallic chemistry.¹ We have demonstrated cleavage of C–H and C–C bonds in the reaction of a trinuclear ruthenium pentahydride complex $\{\text{Cp}^*\text{Ru}(\mu\text{-H})\}_3(\mu_3\text{-H})_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with cyclopentadiene.^{2a} Once a substrate is incorporated into a reaction site in the cluster, even an inert bond could be activated under mild conditions. Both multielectron transfer among the substrate and metal centers and entropy gain by multiple coordination could facilitate the activation of an inert bond in di- and polymetal cluster complexes. Although many stoichiometric and catalytic reactions using cluster complexes have so far been developed,³ it is still uncertain the effect of multiple coordination and

the role of individual metal centers of a cluster complex. We will use the term *multimetallic activation* to refer to a distinctive manner of activation achieved by the concerted interaction among substrates and many metal centers.²

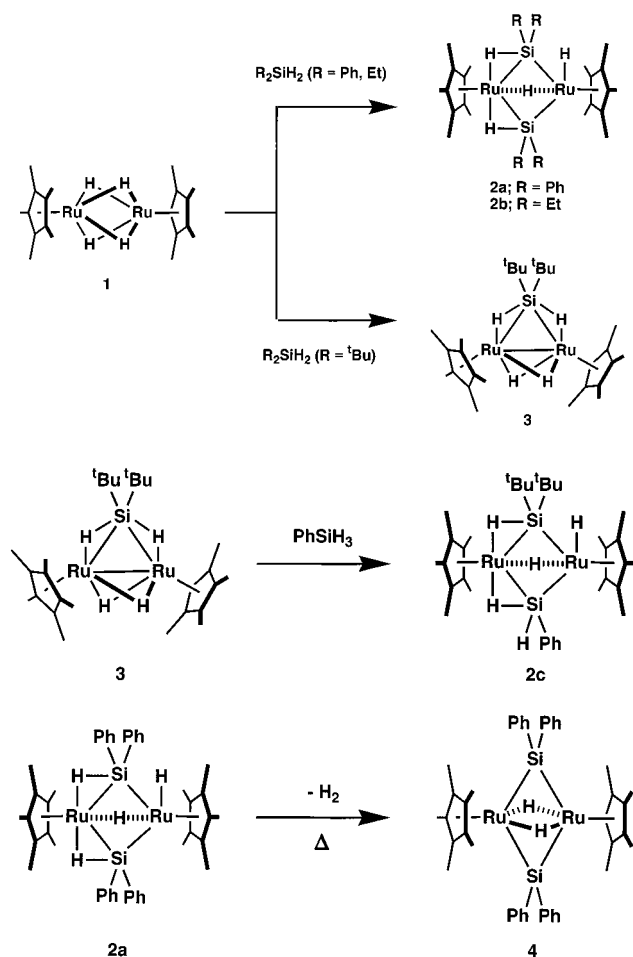
We have demonstrated several examples of multimetallic activation by using ruthenium polyhydride cluster complexes $\{\text{Cp}^*\text{Ru}(\mu\text{-H})\}_3(\mu_3\text{-H})_2$ ² and $\text{Cp}^*\text{Ru}(\mu\text{-H})_4\text{RuCp}^*$ ⁴ as precursors of active species. These complexes can generate multimetallic active species by transferring hydride ligands to a hydride acceptor or by elimination of hydride ligands as dihydrogen. Previously we reported that the reaction of a dinuclear ruthenium tetrahydride complex $\text{Cp}^*\text{Ru}(\mu\text{-H})_4\text{RuCp}^*$ (**1**) with secondary silanes R_2SiH_2 afforded bis(μ -silyl)

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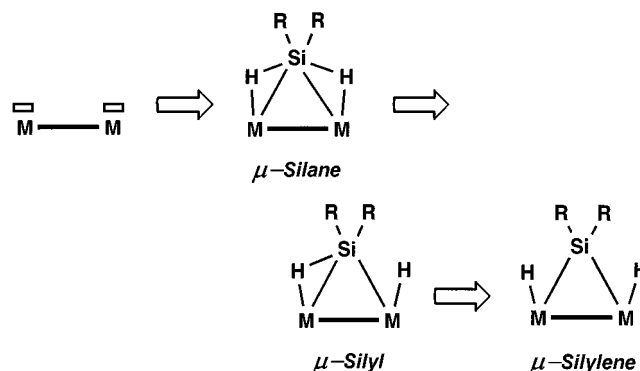
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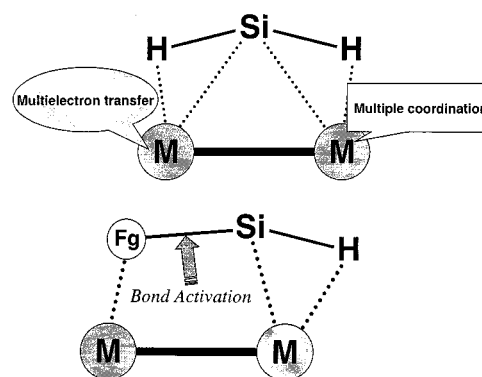
complexes $\{Cp^*Ru(\mu-\eta^2-HSiR_2)\}_2(\mu-H)(H)$ (**2a**, $R = Ph$; **2b**, $R = Et$)^{4g} and a μ -silane complex $\{Cp^*Ru(\mu-H)\}_2(\mu-\eta^2:\eta^2-H_2SiR_2)$ (**3**, $R = tBu$).^{4j} It was characteristic of these complexes that two-electron–three-center ($2e-3c$) interactions were involved in bonding the ruthenium, silicon, and hydride ligand. Such *agostic* $2e-3c$ interactions are often considered to be a “frozen” intermediate for oxidative addition reaction of an Si–H bond,⁵ and actually these $2e-3c$ bonds are thermally cleaved to form Ru–Si σ -bonds. Treatment of **3** with an additional equivalent of a less bulky silane, such as phenylsilane, resulted in formation of a mixed-bridged bis(μ -silyl) complex $(Cp^*Ru)_2(\mu-\eta^2-HSi^tBu_2)(\mu-\eta^2-HSiPhH)(\mu-H)(H)$ (**2c**) via oxidative addition of the η^2 -coordinated Si–H bond.^{4j} The two η^2 -coordinated Si–H bonds of bis(μ -silyl) complex **2a** were subsequently cleaved upon thermolysis to generate a bis(μ -silylene) complex $\{Cp^*Ru(\mu-SiPh_2)(\mu-H)\}_2$ (**4**), but **2b** did not afford the corresponding bis(μ -diethylsilylene) complex.⁴ⁱ The difference in thermal reactivity between **2a** and **2b** probably was due to the substituent effect on the bridging silicon; the electron-withdrawing phenyl group would intensify back-donation from the Ru d-orbital into a $\sigma^*(Si-H)$ -orbital, resulting in the formation of the Ru–Si σ -bond, while the electron-releasing ethyl group has the opposite effect.⁶

In the reactions of **1** with secondary silanes, σ -coordination of the Si–H bond preceded the oxidative addition; that is, formation of the σ -complex is followed by the cleavage of the Si–H bond. Successive cleavage

of two Si–H bonds of a secondary silane affords the μ -silyl complex from a μ -silane complex, and a μ -silylene complex from a μ -silyl complex as shown below. In a series of reactions of **1** with dihydrosilanes, there occurred such stepwise transformation of dihydrosilanes on the dinuclear system, in which it was clearly seen that each ruthenium center acts as a binding site and an activation site. This is a typical example of bimetallic activation.



As mentioned above, the multiple coordination and multielectron transfer would cause the activation of inert bonds. To define the effectiveness of multiple coordination, we use vinylsilanes, which have two types of functional group (Fg), i.e., an Si–H bond and a C=C double bond. Vinylsilanes can coordinate on ruthenium through both the Si–H and C=C bonds, so they apparently are suitable for multiple coordination. As a result of coordination through both the Si–H and C=C bonds, a μ -vinylsilane complex $\{Cp^*Ru(\mu-H)\}_2\{\mu-\eta^2:\eta^2-HSiMe_2-(CH=CH_2)\}$ (**5a**) was obtained by the reaction of **1** with dimethylvinylsilane. Subsequent thermolysis of **5a** resulted in cleavage of the Si–C(sp^2) bond and led to formation of a μ -silylene- μ -ethynyl complex, $(Cp^*Ru)_2(\mu-SiMe_2)(\mu-CCH_3)(\mu-H)$ (**8**). The μ -vinylsilane complex **5a** plays an important role in stepwise Si–H/Si–C bond scission, and these results establish that the bimetallic activation can be achieved by this multiple coordination.



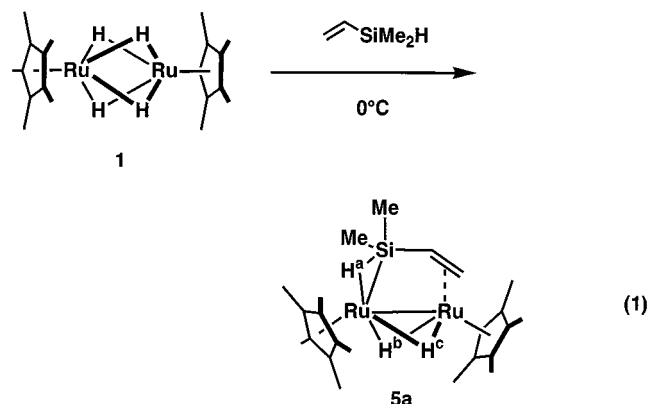
Results and Discussion

Reaction of $Cp^*Ru(\mu-H)_4RuCp^*$ (**1**) with Vinylsilane Having One Si–H Bond. Reaction of tetrahy-

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drude complex $\text{Cp}^*\text{Ru}(\mu\text{-H})_4\text{RuCp}^*$ (**1**) with dimethylvinylsilane $\text{HSiMe}_2(\text{CH}=\text{CH}_2)$ in toluene at 0 °C resulted in quantitative formation of a μ -dimethylvinylsilane complex, $\{\text{Cp}^*\text{Ru}(\mu\text{-H})\}_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HSiMe}_2(\text{CH}=\text{CH}_2)\}$ (**5a**). Complex **5a** was fully characterized on the basis of its



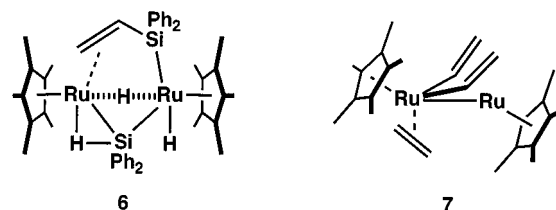
^1H , ^{13}C , and ^{29}Si NMR and IR spectra and FD-MS. An X-ray diffraction study of **5a** established the coordination of dimethylvinylsilane in a $\mu\text{-}\eta^2\text{:}\eta^2$ -mode.

In the ^1H NMR spectrum of **5a** measured at −70 °C, three sharp signals assignable to hydride ligands were observed at δ −9.28 (H^a), δ −14.54 (H^b), and δ −20.22 (H^c), each with an intensity of 1H. These signals broaden and flatten at higher temperature. This strongly indicates a site-exchange process of the hydride ligands, which is discussed later.

The resonances for hydride ligands, H^a , H^b , and H^c , coupled with each other. The values of $J_{\text{H-H}}$ estimated from curve-fitting simulation using the gNMR program are as follows: $J_{\text{Ha-Hb}} = 1.8$ Hz, $J_{\text{Hb-Hc}} = 3.9$ Hz, $J_{\text{Hc-Ha}} = 2.9$ Hz. A set of satellite signals due to coupling with the ^{29}Si nucleus was observed around the signal of H^a (δ −9.28) at −70 °C. Thus, the resonance observed at δ −9.28 was assigned to the hydride of a Ru-H-Si 2e−3c interaction. The $J_{\text{Si-H}}$ value was determined on the basis of the ^{29}Si NMR spectrum measured at −70 °C. The observed $J_{\text{Si-H}}$ value of 54.1 Hz lies in the range of those reported for the 2e−3c interaction among Si, H, and M (20–140 Hz).^{5,7} The 2e−3c Ru-H-Si interaction was also supported by the red-shift of the $\nu_{\text{Ru-H-Si}}$ compared to the $\nu_{\text{Si-H}}$ of the uncoordinated Si-H bond in the IR spectrum. The $\nu_{\text{Ru-H-Si}}$ of **5a** appeared at 1943 cm^{-1} , which was lower than the $\nu_{\text{Si-H}}$ of uncoordinated Si-H bonds (ca. 2100 cm^{-1}), but larger than that for the $\nu_{\text{Ru-H-Si}}$ of the μ -silane complex **3** (1790 cm^{-1}), in which $\mu\text{-}\eta^2\text{:}\eta^2$ -coordination of *tert*-butylsilane has been well defined.^{4j} This is probably due to weak back-donation from the ruthenium centers to $\sigma^*(\text{Si-H})$ in **5a** as compared with that of μ -silane complex **3**.

The ^{29}Si signal of **5a** appeared at δ −8.6, which was at substantially higher field than for bridging silicon ligands. The ^{29}Si signal of the σ -bonded μ -vinylsilyl ligand of $(\text{Cp}^*\text{Ru})_2(\mu\text{-}\eta^2\text{-HSiPh}_2)\{\mu\text{-}\eta^2\text{-SiPh}_2(\text{CH}=\text{CH}_2)\}\text{-(}\mu\text{-H)}(\text{H})$ (**6**)⁴ⁱ was observed at lower field (δ 18.5) in comparison with that of **5a**. Such a high-field shift most likely is due to η^2 -coordination of the Si-H bond. The same trend also was observed between μ -silane and μ -silyl complexes; the ^{29}Si signal of μ -di-*tert*-butylsilane

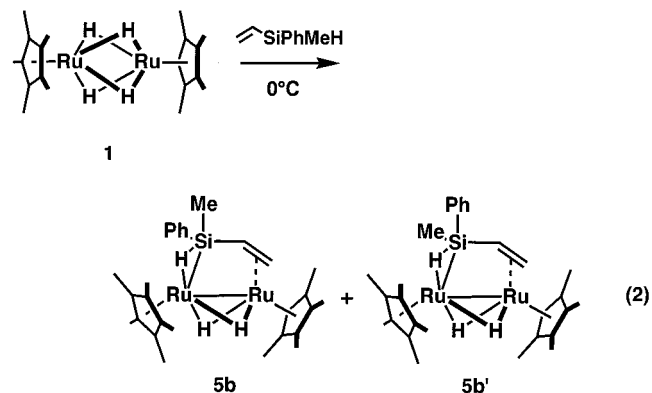
complex $\{\text{Cp}^*\text{Ru}(\mu\text{-H})\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}^i\text{Bu}_2\text{SiH}_2)$ (**3**; δ 75.5) appeared in the high-field region compared to that of the μ -di-*tert*-butylsilyl ligand of the mixed-bridged bis- $(\mu\text{-di-}^i\text{Bu}_2\text{silyl}; \mu\text{-diphenylsilyl})$ complex $(\text{Cp}^*\text{Ru})_2\text{-(}\mu\text{-}\eta^2\text{-HSi}^i\text{Bu}_2)(\mu\text{-}\eta^2\text{-HSiPh}_2)(\mu\text{-H)}(\text{H})$ (**2c**; δ 115.4 for Si^iBu_2).^{4j} The $J_{\text{Si-H}}$ measured at −70 °C was 54.1 Hz, while that value was reduced to 31.0 Hz at 23 °C, which also implies the existence of a site-exchange process of the hydrides, and the $J_{\text{Si-H}}$ of 31.0 Hz measured at 23 °C means the average value among $J_{\text{Si-Ha}}$, $J_{\text{Si-Hb}}$, and $J_{\text{Si-Hc}}$.



The signals for Cp^* ligands in **5a** were observed at δ 1.87 (s, 15H) and 1.51 (s, 15H) in the ^1H NMR spectrum. In the ^1H NMR spectrum of **5a** measured at 23 °C in toluene- d_8 , signals for the vinyl group appeared at δ 4.50 (dd, 1H, $-\text{CH}=\text{CH}_2$), δ 3.87 (d, 1H, $-\text{CH}=\text{CH}_2$), and δ 3.72 (d, 1H, $-\text{CH}=\text{CH}_2$). These shifts were significantly lower than those of the μ -vinylsilyl ligand of **6** (δ 1.44, 1.83, and 1.99)⁴ⁱ and those of the coordinated ethylene in $\{\text{Cp}^*\text{Ru}(\mu\text{-}\eta^2\text{-CH}=\text{CH}_2)\}_2(\eta^2\text{-CH}_2=\text{CH}_2)$ (**7**; δ 1.86).^{4h} This suggests that back-donation from the ruthenium center is relatively reduced in **5a** and the $\text{C}=\text{C}$ bond is coordinated to the ruthenium center somewhat weakly. This is consistent with the downfield shifts of the ^{13}C resonances for vinylic carbons in **5a** and the short Ru-C bond length revealed by the X-ray diffraction studies on **5a**.

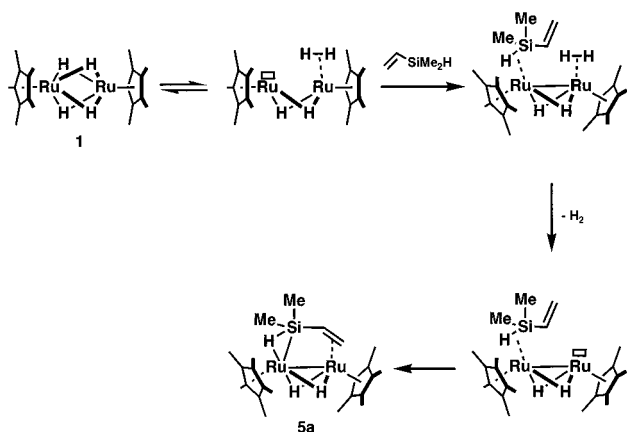
The ^{13}C NMR signals for the coordinated vinyl group of the μ -vinylsilane ligand were also observed at lower field, δ 62.7 (t, $J_{\text{C-H}} = 154.1$ Hz, $-\text{CH}=\text{CH}_2$) and δ 68.0 (d, $J_{\text{C-H}} = 136.1$ Hz, $-\text{CH}=\text{CH}_2$), respectively, than those of the μ -vinylsilyl ligand of **6**, δ 55.7 ($-\text{CH}=\text{CH}_2$) and δ 48.3 ($-\text{CH}=\text{CH}_2$),⁴ⁱ and the coordinated ethylene ligand of **7**, δ 48.9.^{4h}

Two diastereomers, **5b** and **5b'**, were obtained by the reaction of **1** with a slight excess of $(\pm)\text{-HSiPhMe}(\text{CH}=\text{CH}_2)$ in toluene at 0 °C (eq 2). The product ratio **5b/5b'**



was estimated as 56:44 on the basis of the ^1H NMR spectrum measured at 23 °C. The ratio of these diastereomers was not changed on heating the mixture.

Scheme 1



This fact strongly indicates this reaction is kinetically controlled and **5b** is a sterically favored isomer. Although isolation of these two diastereomers has not yet been done, well-separated ^1H NMR signals distinguish these diastereomers from each other. While signals for Cp^* , hydride, and vinyl protons of each isomers were very closely observed, signals for the substituent groups on the bridging silicon appeared separately. This peak separation can be attributed to the ring current shielding effect of the Cp^* ligand; that is, the methyl resonance of the *axial* position on the silicon was observed at higher region than that of the *equatorial* methyl group. Thus, we assigned the methyl signals observed at δ 0.30 to **5b** (*axial*) and δ 0.68 to **5b'** (*equatorial*), respectively.

The ^{29}Si signal of **5b** and **5b'** appeared in high field as that of **5a**, at δ -11.7 and -2.9, respectively. The $J_{\text{Si-H}}$ values measured at 23 $^\circ\text{C}$, 38.9 Hz for **5b** and 39.0 Hz for **5b'**, strongly indicate 2e-3c interactions among Ru, Si, and H.

Reaction Mechanism of 1 with Dimethylvinylsilane. The reaction of $\text{Cp}^*\text{Ru}(\mu\text{-H})_4\text{RuCp}^*$ (**1**) with dimethylvinylsilane was monitored by means of ^1H NMR at -15 $^\circ\text{C}$. Complex **1** slowly reacted with vinylsilane to give **5a** exclusively, and liberation of hydrogen. This was confirmed on the basis of the signal at δ 4.51. During the reaction no intermediate or dimethylethylsilane could be detected. When the reaction was carried out using **1-d**₄ and $\text{DSiMe}_2(\text{CH}=\text{CH}_2)$, incorporation of deuterium into the vinyl group was not observed. This result shows that insertion of the vinyl group into the Ru-H bond was negligible and suggests that coordination of the Si-H bond of dimethylvinylsilane preceded coordination of the vinyl group. Thus, the reaction most likely proceeded as shown in Scheme 1. Two hydride ligands eliminate as dihydrogen followed by coordination of the Si-H bond of dimethylvinylsilane. This hydrogen elimination seems to proceed associatively. In this reaction, it can be seen that dimethylvinylsilane plays the role of a trapping reagent for the dinuclear coordinatively unsaturated species as di-*tert*-butylsilane did.

Treatment of **1-d**₄ with 5.0 equiv of $\text{HSiMe}_2(\text{CH}=\text{CH}_2)$ yielded a partially deuterated μ -vinylsilane complex in which the H/D ratio of the hydride ligand was estimated at 86:14. The H/D ratio was much larger than the anticipated value (H/D = 1:2) from the reaction path shown in Scheme 1. This result shows that an inter-

molecular H/D exchange reaction occurred between **5a** and the remaining excess $\text{HSiMe}_2(\text{CH}=\text{CH}_2)$. This hydride exchange reaction was carried out only between Si-H and Ru-H, and elimination of coordinated vinylsilane was not observed. This was confirmed by the reaction of **5a** with a large excess of $\text{HSiPhMe}(\text{CH}=\text{CH}_2)$. This reaction did not afford μ -phenylmethylvinylsilane complexes **5b** and **5b'** at ambient temperature, and the reaction of the mixture of **5b** and **5b'** with $\text{HSiMe}_2(\text{CH}=\text{CH}_2)$ also did not afford **5a**.

Fluxional Behavior of the μ - η^2 : η^2 -Dimethylvinylsilane Complex. While hydride signals of **5a**, H^a , H^b , and H^c , were observed as three sharp signals at -70 $^\circ\text{C}$, they broadened and flattened at higher temperature and coalesced into one signal at 30 $^\circ\text{C}$, which implies the site-exchange of the hydride ligands in complex **5a** (Figure 1). From the line-shape analysis of the variable-temperature ^1H NMR spectra, the ΔG^\ddagger value of this fluxional process was estimated at $12.6 \pm 0.1 \text{ kcal mol}^{-1}$ at 0 $^\circ\text{C}$ ($\Delta S^\ddagger = -0.9 \pm 1.5 \text{ cal mol}^{-1} \text{ K}^{-1}$, $\Delta H^\ddagger = 12.4 \pm 0.4 \text{ kcal mol}^{-1}$). Since all three signals broadened simultaneously, their site-exchange occurred randomly, and the rates of the individual site-exchange process, i.e., H^a/H^b , H^b/H^c , H^c/H^a , were probably equal. Actually, simulated signals obtained by using the same k values fit well to the recorded spectra. This site-exchange of hydride ligands most likely proceeds via the μ -silyl intermediate **A** shown in Scheme 2, which was formed by oxidative addition of the σ -coordinated Si-H bond. Similar ΔS^\ddagger and ΔH^\ddagger values were obtained from a VT-NMR study of a mixture of diastereomers $\{\text{Cp}^*\text{Ru}(\mu\text{-H})_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HSiPhMe}(\text{CH}=\text{CH}_2)\}\}$ (**5b** and **5b'**; for **5b**, $\Delta S^\ddagger = -2.3 \pm 0.8 \text{ cal mol}^{-1} \text{ K}^{-1}$, $\Delta H^\ddagger = 12.1 \pm 0.2 \text{ kcal mol}^{-1}$, for **5b'**, $\Delta S^\ddagger = -0.6 \pm 0.7 \text{ cal mol}^{-1} \text{ K}^{-1}$, $\Delta H^\ddagger = 12.3 \pm 0.2 \text{ kcal mol}^{-1}$).

The signals of Me groups on the bridging silicon in **5a** broadened above 30 $^\circ\text{C}$, which means that there is another fluxional process including inversion of the H-Si-C=C moiety at higher temperature (Scheme 3). Two sharp signals assignable to methyl groups on the bridging silicon were observed at δ 0.45 and 0.05 at -30 $^\circ\text{C}$.

While the line-widths at half-height of those signals $W_{1/2}$ were 1.4 Hz at -30 $^\circ\text{C}$, they increased to 6.4 Hz at 50 $^\circ\text{C}$. Though we could not simulate this behavior accurately due to a concomitant gradual thermolysis of **5a** that occurred above room temperature (vide infra), the ΔG^\ddagger value was roughly estimated at ca. $15.8 \pm 0.4 \text{ kcal mol}^{-1}$ at 0 $^\circ\text{C}$ ($\Delta S^\ddagger = -24.5 \pm 3.9 \text{ cal mol}^{-1} \text{ K}^{-1}$, $\Delta H^\ddagger = 9.2 \pm 1.2 \text{ kcal mol}^{-1}$). The large negative ΔS^\ddagger value compared to that for the hydride site-exchange process implies that this process requires a more sterically restricted transition state. In the case of the μ - η^2 : η^2 -phenylmethylvinylsilane complexes **5b** and **5b'**, the **5b/5b'** ratio did not change on heating at 70 $^\circ\text{C}$. While two methyl groups on the silicon of **5a**, *axial* and *equatorial*, exchanged their positions by inversion of the H-Si-C=C moiety, isomerization between **5b** and **5b'** was not observed at any temperature. Isomerization between the two diastereomers, **5b** and **5b'**, likely occurs as a result of inversion of the H-Si-C=C moiety. Lack of isomerization seems to be due to the influence of one phenyl group on the silicon; that is, the electron-withdrawing character of the phenyl group increases the

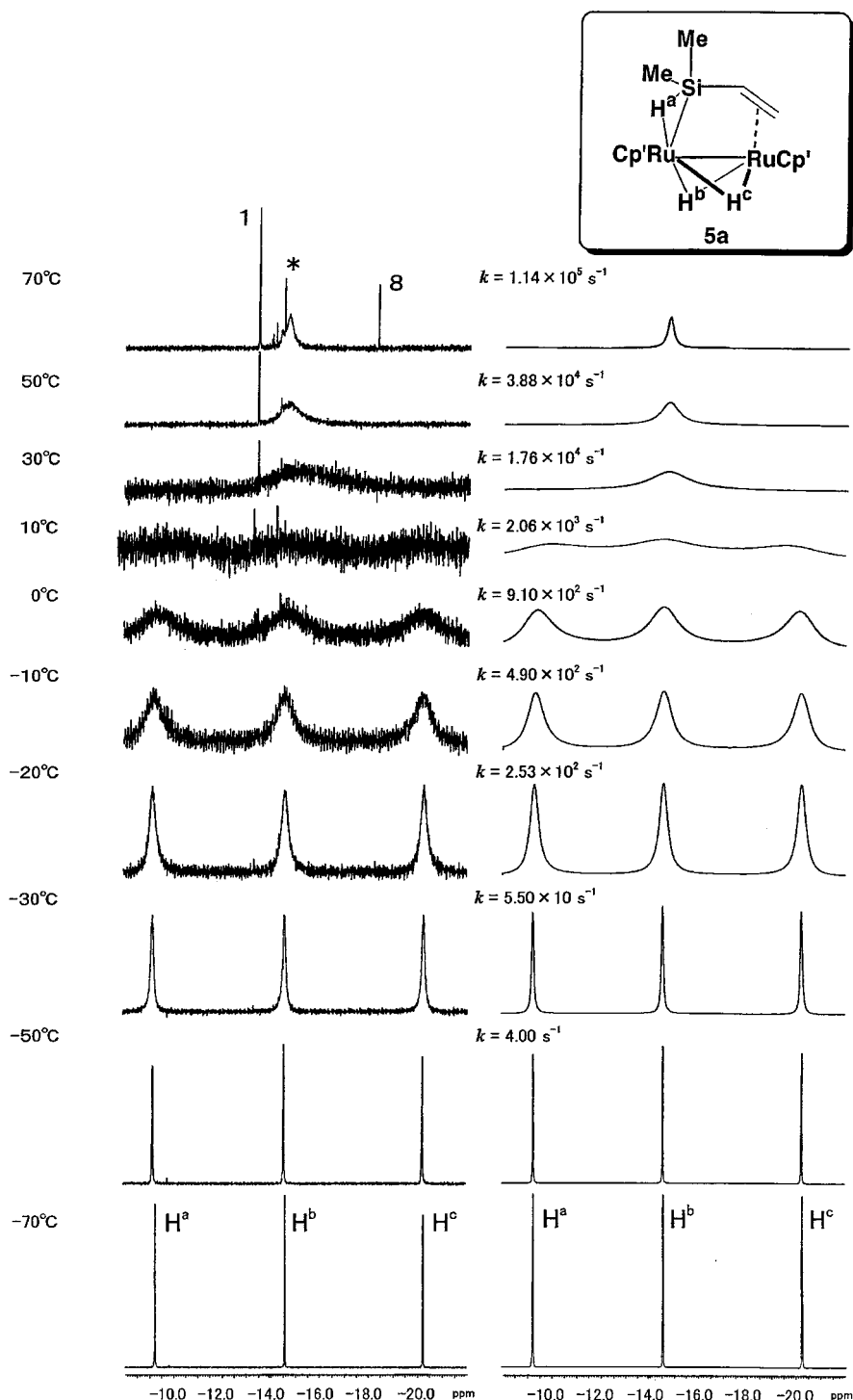


Figure 1. Variable-temperature ^1H NMR spectra of $\{\text{Cp}^*\text{Ru}(\mu\text{-H})\}_2\{\mu\text{-}\eta^2\text{-}\eta^2\text{-HSiMe}_2(\text{CH}=\text{CH}_2)\}$ (**5a**) showing hydride signals (left) and results of simulation (right). In the recorded spectrum at 70 °C, newly produced signals were found. **1** and **8** mean hydride signals of $\text{Cp}^*\text{Ru}(\mu\text{-H})_4\text{RuCp}^*$ and $(\text{Cp}^*\text{Ru})_2(\mu\text{-SiMe}_2)(\mu\text{-CMe})(\mu\text{-H})$, respectively. They are produced by the thermolysis of **5a**. Asterisk signal represents thermally produced unidentified compounds.

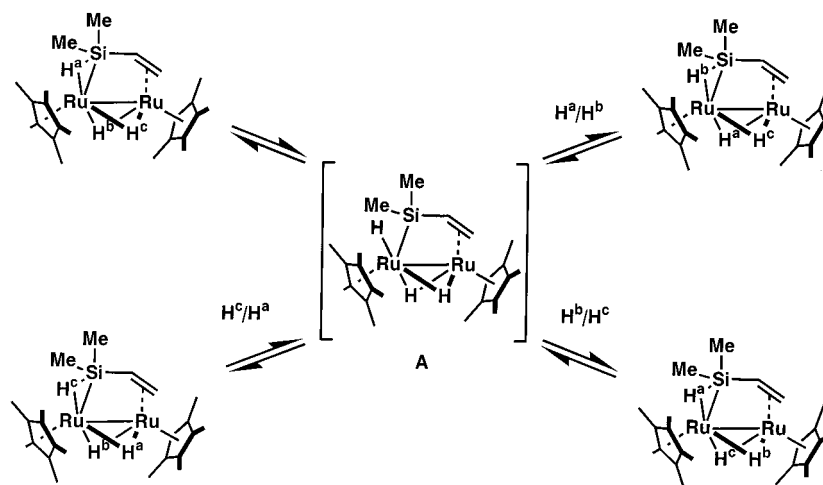
back-donation from the ruthenium center and strengthens the Ru–Si bond.

X-ray Crystal Structure of the μ -Vinylsilane Complex **5a.** The structure of **5a** was determined by X-ray crystallography using a single crystal obtained from heptane at -20 °C. The structure of **5a**, shown in Figure 2, establishes the unique $\mu\text{-}\eta^2\text{:}\eta^2$ geometry of the $\text{HSiMe}_2(\text{CH}=\text{CH}_2)$. The crystal data for **5a** are given in the Experimental Section (Table 4), and the selected bond lengths and bond angles are listed in Table 1.

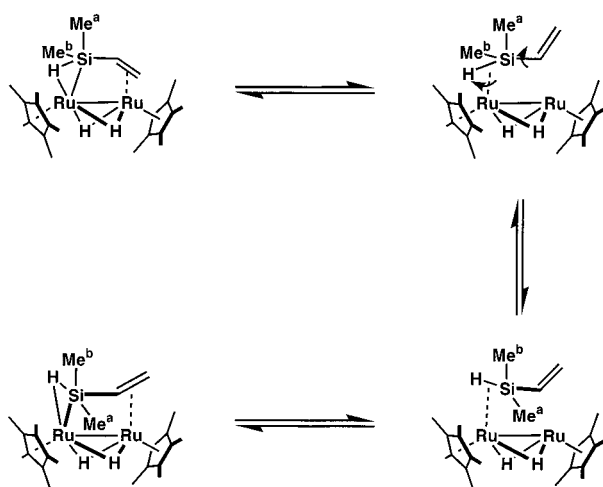
One of the three hydride ligands of **5a**, $\text{H}(3)$, is bridged between Ru(1) and Si, forming the $2e\text{--}3c$ interaction. The Si–H(3) distance, 1.68(6) Å, is reasonably longer than those reported for organosilicon compounds (1.48 Å).⁸ This supports the decrease in the bonding interaction between Si and H by σ -coordination to Ru(1).

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Scheme 2



Scheme 3



Although X-ray crystallography is not the best method to determine the location of the H atom attached to a heavy atom, the observed Si–H bond lengthening is consistent with the reduced $J_{\text{Si-H}}$ coupling obtained by ^1H and ^{29}Si NMR spectroscopy and red-shift of the $\nu_{\text{Si-H}}$ (vide supra). The Ru(1)–Si(1) distance (2.384(2) Å) is slightly shorter than those in the μ -silyl and μ -silane complexes (2.680(3)–2.414(3) Å).^{4g,i,j} The Ru(2)–Si(1) distance of 3.019(2) Å shows that there is no bonding

Table 1. Selected Bond Distances (Å) and Angles (deg) for 5a

| | | | |
|------------------|-----------|------------------|----------|
| Ru(1)–Ru(2) | 2.7300(7) | Ru(2)–C(1) | 2.224(7) |
| Ru(1)–Si | 2.386(2) | Ru(2)–C(2) | 2.212(6) |
| Ru(1)–H(1) | 1.67(5) | Ru(2)–H(1) | 1.85(5) |
| Ru(1)–H(2) | 1.61(6) | Ru(2)–H(2) | 1.96(6) |
| Ru(1)–H(3) | 1.56(4) | C(1)–C(2) | 1.39(1) |
| Si–C(2) | 1.890(7) | Si–C(3) | 1.870(7) |
| Si–C(4) | 1.916(8) | Si–H(3) | 1.66(4) |
| Ru(2)–Ru(1)–Si | 71.97(5) | Ru(1)–Ru(2)–C(1) | 92.1(2) |
| Ru(1)–Ru(2)–C(2) | 84.1(2) | C(1)–Ru(2)–C(2) | 36.5(3) |
| Ru(1)–Si–C(2) | 101.8(2) | Ru(1)–Si–C(3) | 112.7(2) |
| Ru(1)–Si–C(4) | 120.5(3) | C(2)–Si–C(3) | 94(1) |
| C(2)–Si–C(4) | 111.4(4) | C(3)–Si–C(4) | 102.5(3) |
| Ru(2)–C(1)–C(2) | 71.3(4) | Ru(2)–C(2)–C(1) | 72.2(4) |
| Si–C(2)–C(1) | 122.4(6) | | |

interaction between Si and Ru(2). Other hydrides, H(1) and H(2), are found between two rutheniums.

The bond lengths and angles of the coordinated vinyl group are almost the same as those of coordinated alkenes that have previously been reported; the C(1)–C(2) distance (1.39(1) Å) is in the range of normal C=C double bonds, but it is shorter than the C–C distance of the coordinated ethylene in $\{\text{Cp}^*\text{Ru}(\mu\text{-}\eta^2\text{-CH=CH}_2)\}_2$ ($\eta^2\text{-CH}_2\text{=CH}_2$) (**7**) by ca. 0.08 Å.^{4b} The Ru(2)–C(1) and Ru(2)–C(2) distances (2.228(7) and 2.218(6) Å, respectively) are longer than the Ru–C distances of the coordinated ethylene in **7** by ca. 0.06 Å. These results and NMR data for the coordinated vinyl group strongly suggest that the π -coordination of the vinyl group in dimethylvinylsilane to Ru(2) was considerably weakened.

Thermolysis of μ -Vinylsilane Complex 5a; Si–C Bond Cleavage Leading to a μ -Silylene- μ -Ethyldiene Complex. There have been few examples of oxidative addition of a Si–C bond to a metal center.⁹ Sakaki et al. theoretically investigated the oxidative

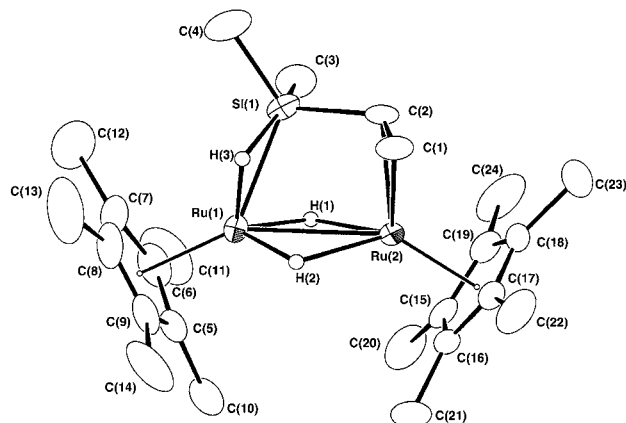
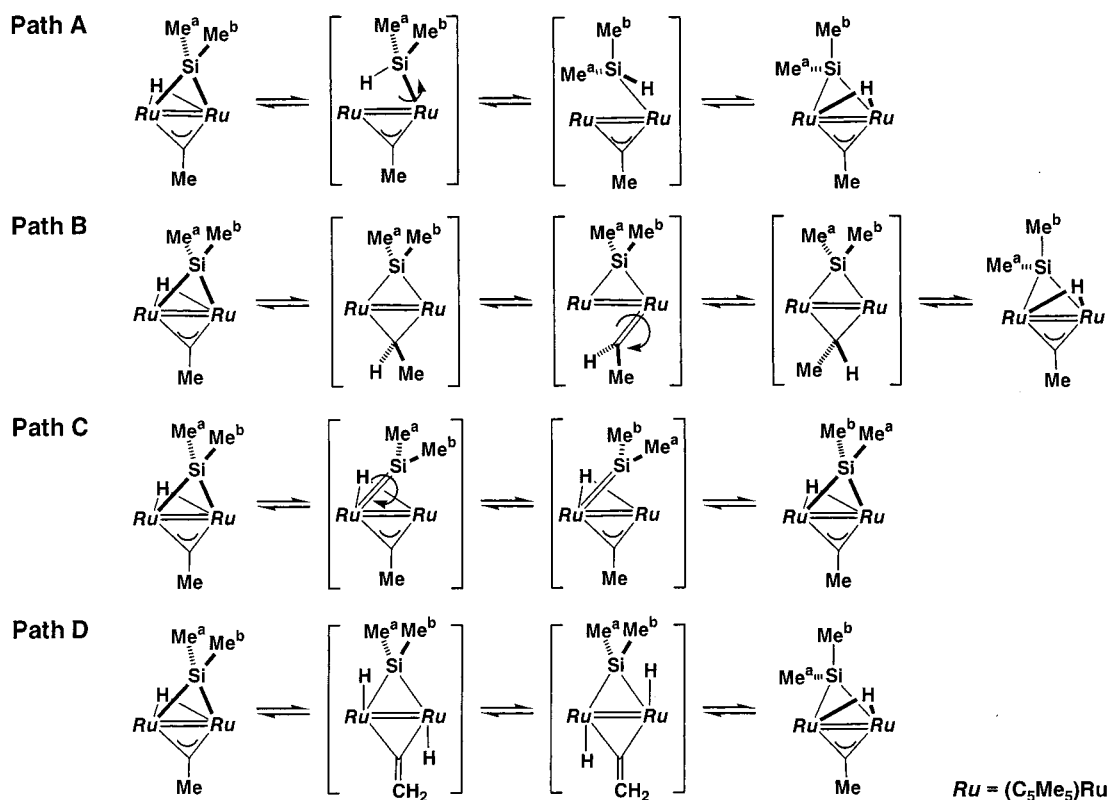


Figure 2. Molecular structure of $\{\text{Cp}^*\text{Ru}(\mu\text{-H})_2\}_2\{\mu\text{-}\eta^2\text{-}\eta^2\text{-HSiMe}_2(\text{CH=CH}_2)\}$ (**5a**), with thermal ellipsoids at 30% probability level.

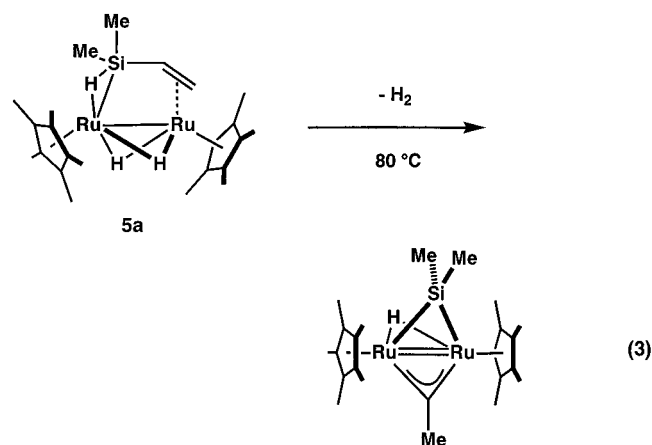
- (9) (a) Thomson, S. K.; Young, G. B. *Organometallics* **1989**, *8*, 2068. (b) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462. (c) Lin, W.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1993**, *115*, 3022. (d) Lin, W.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 2309. (e) Shelby, Q. D.; Lin, W.; Girolami, G. S. *Organometallics* **1999**, *18*, 1904. (f) Hofmann, P.; Heiss, H.; Neiteler, P.; Müller, G.; Lachmann, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 880. (g) Kakiuchi, F.; Furuta, K.; Murai, S. *Organometallics* **1993**, *12*, 15. (h) Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 419. (i) Akita, M.; Hua, R.; Nakanishi, S.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1997**, *16*, 5572. (j) Hua, R.; Akita, M.; Moro-oka, Y. *Chem. Commun.* **1996**, 541.

Scheme 4



addition of Si-X (X = H, F, C, and Si) to the $Pt(PH_3)_2$ fragment by the ab initio MO/MP4 method and demonstrated that the activation energy of the Si-Si and the Si-C oxidative addition is greater than that of the Si-H oxidative addition.¹⁰ The high activation energy is ascribed to the requirement for turning the direction of the sp^3 orbital of the carbon atom to a metal center. Unlike most mononuclear complexes, a cluster complex most probably activates even an Si-C bond due to the cooperative action of adjacent metal centers if the silane molecule has functionality capable of coordination to the metal centers. Multiple coordination of a substrate to the multimetallic centers brings about an entropic advantage in the bond-breaking reaction.

Thermolysis of complex **5a** at 80 °C afforded a μ -silylene, μ -ethylidyne complex $(Cp^*Ru)_2(\mu-SiMe_2)(\mu-CCH_3)(\mu-H)$ (**8**) in 70% yield via Si-C(sp^2) bond cleavage (eq 3). Complex **8** was fully characterized by means of



1H , ^{13}C , and ^{29}Si NMR and IR spectral data and FD-MS, as well as analytical data. The structure of **8** was unambiguously determined by means of X-ray diffraction study (vide infra). The X-ray study established a dinuclear structure bridged by a silylene and an ethylidyne ligand as a result of Si-C bond cleavage followed by insertion of the C=C double bond into one of the Ru-H bonds. In the ^{13}C NMR spectrum of **8**, the ethylidyne carbon atom signal was observed at very low field (δ 387.7), and the methyl group resonance of the ethylidyne ligand was found at δ 3.95 as a singlet in the 1H NMR spectrum. Both NMR data distinctively show the bridged ethylidyne structure of **8**. The ^{29}Si signal of the μ -silylene ligand of **8** was observed at low field (δ 197.8), the typical value for a μ -silylene ligand. The signals of the hydride ligand and Cp^* were observed at δ -17.94 and 1.76 as sharp peaks in the 1H NMR spectrum at any temperature, respectively.

The signals of the methyl groups of **8** were observed at δ 0.66 and 1.70 as broad peaks in the 1H NMR spectrum measured at 10 °C. They became a set of two sharp signals at lower temperature and coalesced into one signal at 60 °C. The activation energy ΔG^\ddagger of this fluxional process calculated at the coalescence temperature was estimated at ca. 15.0 kcal mol⁻¹ ($\Delta S^\ddagger = -7.7 \pm 0.4$ cal mol⁻¹ K⁻¹, $\Delta H^\ddagger = 12.5 \pm 0.1$ kcal mol⁻¹). The exchange of two methyl signals on bridging silicon can be accounted for by the processes A-D shown in Scheme 4; paths A-D are the mechanisms that involve μ -silyl, terminally bonded ethylidyne, terminally bonded silylene, and μ -vinylidene intermediates, respectively.

Formation of the μ -ethylidene ligand was confirmed by the reaction of **8** with carbon monoxide (vide infra).

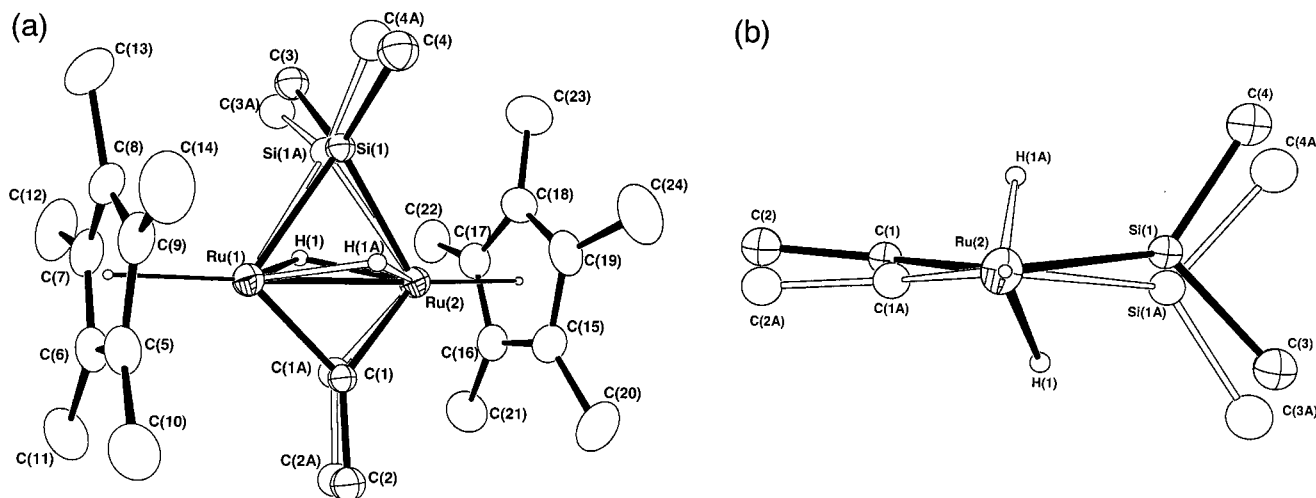


Figure 3. (a) Molecular structure of $(\text{Cp}^*\text{Ru})_2(\mu\text{-SiMe}_2)(\mu\text{-CCH}_3)(\mu\text{-H})$ (**8**), with thermal ellipsoids at 30% probability level. The crystal submitted to the diffraction studies included the form of **8** that is 44.3% disordered about the hydride position, which is drawn by a white line. (b) View of the Ru_2SiC core of **8** along the Ru–Ru axis.

Reversible transformation between a bridging and terminally bonded alkylidene has often been proposed for isomerization reactions of dinuclear complexes.¹¹ A few examples of transformation of bridging to the terminal alkylidene have been reported.¹² Rotation of the terminal alkylidene ligand around the $\text{M}=\text{C}$ bond has been well investigated, and the activation energy ΔG^\ddagger of the rotation is $10.4 \text{ kcal mol}^{-1}$ for $(\text{C}_5\text{H}_5)\text{Fe}(\text{dppm})(=\text{CH}_2)$.¹³

As for the μ -silylene ligand, while there was no isolated example of the transformation of bridging to the terminal silylene ligand, such a rearrangement was proposed in some isomerization reactions.¹⁴ Tilley et al. proposed reversible transformation of a bridging silylene to terminal silylene followed by rotation around the $\text{Ru}=\text{Si}$ bond in the silylene isomerization of $(\text{Cp}^*\text{Ru})_2\{\mu\text{-SiPh(OMe)}\}(\mu\text{-OMe})(\mu\text{-H})$.^{14a} But, the rate of this rearrangement was relatively slow and this isomerization was irreversible; it took more than 24 h at room temperature. Rotation of the terminal silylene around the $\text{M}=\text{Si}$ bond was observed in $(\text{C}_5\text{H}_5)\text{W}(\text{CO})_2\{(\text{SiMe}_2)\cdots\text{NEt}_2\cdots(\text{SiMe}_2)\}$, and the activation parameters were estimated at $\Delta H^\ddagger = 17.4 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = 11.7 \text{ cal mol}^{-1} \text{ K}^{-1}$.¹⁵

Both path B and path C are possible, but when compared to a mononuclear system, they seem to require a more crowded transition state for dinuclear complexes due to the neighboring metal center in their rotation around the $\text{M}=\text{C}$ or $\text{M}=\text{Si}$ bond. So, larger negative ΔS^\ddagger values would be observed.

Hydride migration via a μ -vinylidene intermediate is also possible (path D). A 1,3-shift of the methyl proton of the ethylidyne ligand possibly affords a μ -vinylidene intermediate. Incorporation of deuterium into the meth-

yl group of the ethylidyne ligand during the H/D exchange reaction (vide infra) indicates that site-exchange between the hydride and methyl proton of the ethylidyne ligand takes place. Irradiation of the methyl protons of the μ -ethylidyne ligand at 50°C resulted in a 10% decrease of the intensity of the hydride resonance, but the rate of hydride migration was considerably slower than the estimated value by the line-shape analysis ($k = 77.2 \text{ s}^{-1}$). Thus, the fluxionality of two methyl groups on the silicon atom could not be explained by the μ -vinylidene mechanism D.

Path A involves reductive elimination between μ -silylene and hydride followed by a swing around the Ru–Si bond. Eisenberg et al. proposed a rapid reductive elimination/oxidative addition mechanism for the fluxional process of the dirhodium μ -silylene complex $\text{Rh}_2\text{H}_2(\mu\text{-SiPhH})(\text{CO})_2(\text{dppm})_2$.¹⁶ The ΔG^\ddagger value was calculated to be $12 \pm 1 \text{ kcal mol}^{-1}$ both at -30°C and at 25°C , which indicated a very small ΔS^\ddagger for the process. Similarly, rotation around the Ru–Si bond of the μ -silyl group formed by the reductive elimination of μ -silylene with the hydride of complex **8** followed by the oxidative addition should move the hydride ligand from the bottom to the upper side of the Ru_2SiC moiety. This rearrangement could explain the temperature dependence of NMR signals for the methyl groups on the bridging silicon atom and is consistent with the very small ΔS^\ddagger value. So, it was assumed that the fluxionality of **8** was most probably due to path A.

The X-ray diffraction study was carried out using a red-brown single crystal of **8** obtained from cold toluene/pentane mixed solution. The structure of **8** is shown in Figure 3, and selected bond lengths and angles are listed in Table 2. Disordered atoms, Si(1), C(1), C(2), C(3), and C(4), were refined isotropically. Location of the hydride ligands was determined in the differential Fourier map and refined isotropically.

The Ru(1)–Ru(2) distance of $2.5888(15) \text{ \AA}$ corresponds to a Ru–Ru double bond and is consistent with the bond order between Ru atoms anticipated from the EAN rule applied to **8**. The small Ru(1)–Si(1)–Ru(2) angle

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Table 2. Selected Bond Distances (Å) and Angles (deg) for **8**

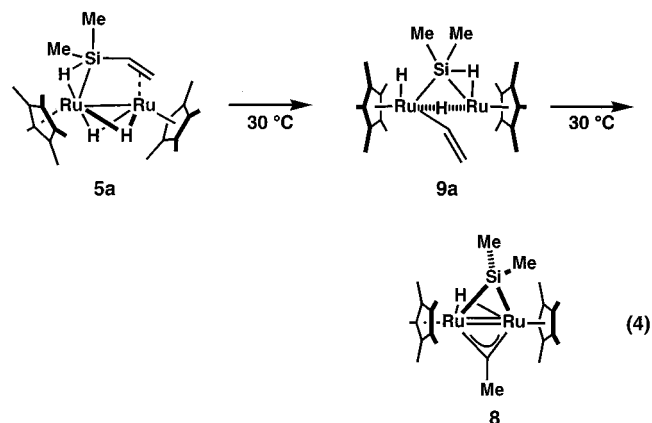
| | | | |
|-------------------|------------|-------------------|-----------|
| Ru(1)–Ru(2) | 2.5888(15) | Ru(1)–Si(1) | 2.337(3) |
| Ru(2)–Si(1) | 2.335(3) | Ru(1)–C(1) | 1.913(13) |
| Ru(2)–C(1) | 1.918(13) | Ru(1)–H(1) | 1.78(4) |
| Ru(2)–H(1) | 1.77(4) | Si(1)–C(3) | 1.961(12) |
| Si(1)–C(4) | 1.893(12) | C(1)–C(2) | 1.489(16) |
| Ru(2)–Ru(1)–Si(1) | 56.31(8) | Ru(2)–Ru(1)–C(1) | 47.6(4) |
| Si(1)–Ru(1)–C(1) | 102.8(4) | Ru(1)–Ru(2)–Si(1) | 56.38(8) |
| Ru(1)–Ru(2)–C(1) | 47.4(4) | Si(1)–Ru(2)–C(1) | 102.7(4) |
| Ru(1)–Si(1)–Ru(2) | 67.31(9) | Ru(1)–Si(1)–C(3) | 117.6(4) |
| Ru(1)–Si(1)–C(4) | 122.3(4) | Ru(2)–Si(1)–C(3) | 119.0(4) |
| Ru(2)–Si(1)–C(4) | 121.6(4) | C(3)–Si(1)–C(4) | 105.9(5) |
| Ru(1)–C(1)–Ru(2) | 85.0(5) | Ru(1)–C(1)–C(2) | 136.7(9) |
| Ru(2)–C(1)–C(2) | 138.2(9) | | |

(67.31(9)°) also suggests a strong bonding interaction between rutheniums.¹⁷ Two Cp* ligands are nearly parallel to each other, and centroids of the two Cp* ligands and the ruthenium atoms are located on an almost straight line. The Ru–Si(1) distance of 2.336 Å (av) is in the normal range of the Ru–Si σ -bond, and the relatively short Ru–C(1) distance of 1.916 Å (av) indicates an ethylidyne ligand. The Ru₂SiC moiety is slightly folded; the dihedral angle between Ru(1)–Ru(2)–Si(1) and Ru(1)–Ru(2)–C(1) is 165.7(6)°. Small steric repulsion among C(1), Si(1), and H(1) would cause the divergence from the planarity of the Ru₂SiC moiety. The view along the Ru(1)–Ru(2) axis clearly shows that the ruthenium centers are sterically less crowded.

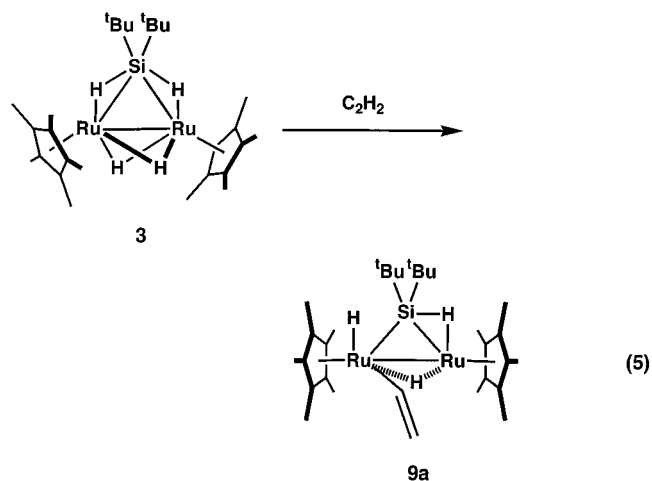
The Si(1)⋯H(1) distance of 2.02(9) Å is considerably short. It is only 10% longer than the η^2 -Si–H distance of 1.802(5) Å of (η^5 -C₅MeH₄)Mn(CO)PMe₃(η^2 -HSiPh₂F) determined by neutron diffraction.¹⁸ H(1), moreover, seemed to lean toward Si(1); the dihedral angle between Ru(1)–Ru(2)–Si(1) and Ru(1)–Ru(2)–H(1) is 76(4)° is considerably smaller than that between Ru(1)–Ru(2)–C(1) and Ru(1)–Ru(2)–H(1) (119(4)°). It is difficult to determine the accurate position of the hydrogen atom attached to transition metals by means of X-ray diffraction studies, but the facts of the relatively short Si(1)⋯H(1) distance and inclination of the Ru–H bond to the Si atom may imply a very weak interaction between Si and H. The $J_{\text{Si-H}}$ value of 22.7 Hz was in the gray zone between $^1J_{\text{Si-H}}$ of the 2e–3c Si–H interaction and $^2J_{\text{Si-H}}$ of the silyl hydride complexes, but it seems to imply a weak interaction, too. It cannot be concluded from both this X-ray study and NMR data, but if there were some kind of interaction between H and Si, the fluxional behavior of **8** could be well documented by path A in Scheme 4.¹⁹

Cleavage of the Si–C(vinyl) bond of **5a** was monitored in a sealed tube by means of ¹H NMR spectroscopy at

lower temperature (30 °C). Complex **5a** was completely consumed after 80 h. Generation of an intermediary μ -silyl, μ -vinyl complex (Cp*Ru)₂(μ - η^2 -HSiMe₂)(μ -CH=CH₂)(μ -H)(H) (**9a**) was observed at the beginning (eq 4),



and the concentration of **9a** was maximized after 12 h (ca. 20%). Complex **9a** was characterized on the basis of the ¹H and ²⁹Si NMR spectra. The spectra were very similar to those of the analogous μ - η^2 -silyl, μ - η^1 : η^2 -vinyl complex, (Cp*Ru)₂(μ - η^2 -HSi^tBu₂)(μ -CH=CH₂)(μ -H)(H) (**9b**), which was independently prepared by the reaction of μ -silane complex **3** with acetylene (eq 5; see Experimental Section). In the ¹H NMR spectra of the reaction



mixture after 12 h, two singlets assignable to Cp* of **9a** were observed at δ 1.69 and 2.00. The signals of vinyl groups appeared at δ 6.71 (dd, J = 10.8, 7.6 Hz), δ 3.17 (dd, J = 7.6, 2.4 Hz), and δ 3.08 (dd, J = 10.8, 2.4 Hz). The signals for the hydride ligands were found as 2:1 of two peaks at δ –14.10 and –13.19, in which the signal found at δ –13.19 was broadened at lower temperature. The ²⁹Si signal of the bridging silicon ligand was found at δ 71.5 with a 59.6 Hz coupling constant between the hydride at –70 °C, which strongly indicated a 2e–3c interaction between Ru, Si, and hydride.

As the concentration of complex **9a** decreased, generation of both μ -silylene, μ -ethylidyne complex **8** and tetrahydride complex **1** began to be observed. After 80 h, the ratio between **8** and **1** reached 80:20. The yield of **8**(+**1**) was estimated at 70% on the basis of the ¹H NMR spectra. The formation of **1** can be explained by the reaction of **8** with the liberated dihydrogen (vide infra).

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(19) The bond distance for Si(1A)⋯H(1A) (2.27(7) Å) is slightly longer than Si(1)⋯H(1). The dihedral angles C(1A)–Ru(1)–Ru(2)–Si(1A), C(1A)–Ru(1)–Ru(2)–H(1A), and Si(1A)–Ru(1)–Ru(2)–H(1A) are 169.6(9)°, 102(3)°, and 88(3)°, respectively. These values are slightly different from the structure with high occupancy, but still imply weak interaction between the hydride and the bridging silicon atom. We are now investigating the presence of this agostic interaction between Si and H by MO calculation and will report in due course.

Two mechanisms can be possible for the Si–C(sp²) bond cleavage; one is *direct oxidative addition*, and the other is a *β -Si elimination mechanism*. Wakatsuki et al. showed a Si–C scission via β -Si elimination in the reaction of a vinylsilane with a ruthenium hydride complex,²⁰ and several groups reported synthesis of silylated alkenes by β -Si elimination.²¹ The formation of **9a** could be rationalized considering an oxidative addition of a C–H bond of the coordinated ethylene that was generated by insertion of a vinyl group into a Ru–H bond followed by β -Si elimination. We consider, however, it is a case of an oxidative addition of a Si–C bond because the Si–C bond of triphenylsilane was also cleaved upon the reaction of **1**, yielding bis- μ -diphenylsilylene complex **4** and benzene.²²

Intermolecular H/D Exchange Reaction between **8 and Benzene-*d*₆.** μ -Silylene, μ -ethyldiyne complex **8** was stable in even refluxing toluene for several days. Although **8** did not show any decomposition in C₆D₆ at 100 °C in a sealed NMR tube, H/D exchange reaction between **8** and C₆D₆ took place. It causes a slight change in the ¹H NMR signal for the methyl group of the ethyldiyne ligand as well as disappearance of the hydride signal. Incorporation of deuterium into the methyl group of the ethyldiyne ligand was shown by the observation of a 1:1:1 triplet signal assignable to μ -CCH₂D, which newly appeared beside the signal of the methyl proton of the μ -ethyldiyne ligand in 10 h. Prolonged heating resulted in appearance of another 1:2:3:2:1 quintet signal assignable to μ -CCHD₂, as shown in Figure 3. ²H NMR measurements on this sample clearly showed incorporation of deuterium into both the methyl group and hydride site. This result indicates occurrence of aromatic C–H bond activation as well as a hydride site-exchange process via path D in Scheme 4, i.e. hydride migration via a μ -vinylidene intermediate.

Incorporation of deuterium into the methyl group of the η^5 -pentamethylcyclopentadienyl ligand also was observed by means of ²H NMR, which indicates reversible C–H bond scission/formation of the methyl group via a fulvene intermediate. While deuterium was incorporated into μ -ethyldiyne, Cp*, and hydride sites, incorporation into methyl groups on the bridging silicon was not observed.

This H/D exchange reaction seemed to be derived from the coordinatively unsaturated character of **8**. Electron deficiency of the ruthenium center would require an intra- and/or intermolecular σ -coordination of the C–H bond.

The Reaction of Cp*Ru(μ -H)₄RuCp* (**1**) with Trimethylvinylsilane; Formation of μ -Silylene,

(20) (a) Wakatsuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703. (b) Wakatsuki, Y.; Yamazaki, H. *J. Organomet. Chem.* **1995**, 500, 349. (c) Mise, T.; Takaguchi, Y.; Umemiya, T.; Shimizu, S.; Wakatsuki, Y. *Chem. Commun.* **1998**, 699.

(21) See for example: (a) Yi, C. S.; He, Z.; Lee, D. W.; Rheingold, A. L.; Lam, K.-C. *Organometallics* **2000**, 19, 2036. (b) Kakiuchi, F.; Yamada, A.; Chatani, N.; Murai, S.; Furukawa, N.; Seki, Y. *Organometallics* **1999**, 18, 2033. (c) Marciniak, B.; Pietraszuk, C. *Organometallics* **1997**, 16, 4320. (d) Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, 27, 289.

(22) Bis- μ -diphenylsilylene complex {Cp*Ru(μ -SiPh₂)(μ -H)} (**4**) was obtained by the reaction of Cp*Ru(μ -H)₄RuCp* with triphenylsilane with liberating benzene. Takao, T.; Amako, M.; Tanaka, M.; Suzuki, H. Manuscript in preparation.

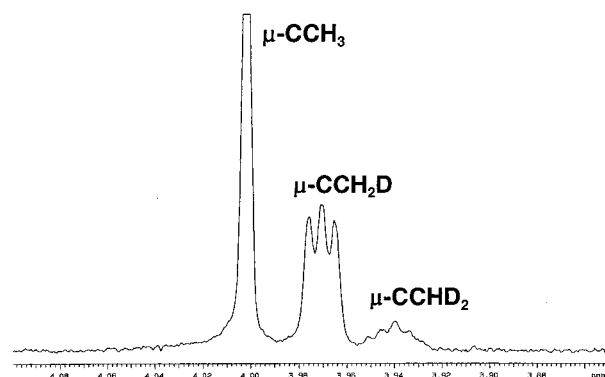
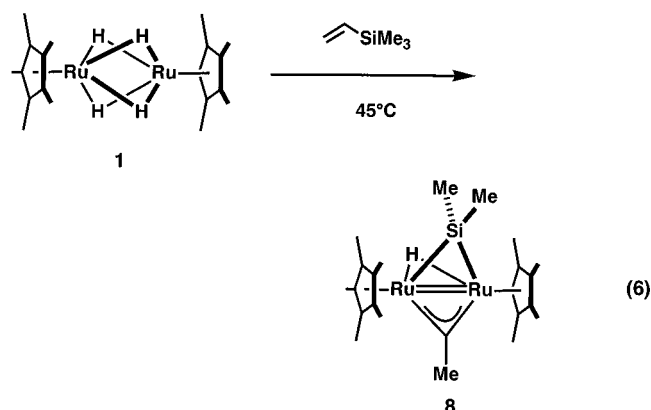


Figure 4. ¹H NMR spectra of the methyl group of the μ -ethyldiyne ligand in the H/D exchange reaction of **8** with benzene-*d*₆ at 100 °C after 48 h.

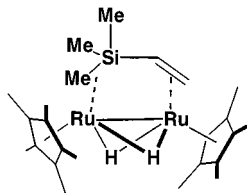
μ -Ethyldiyne Complex via Si–C/Si–C Bond Cleavage. The reaction of Cp*Ru(μ -H)₄RuCp* (**1**) with a vinylsilane having no Si–H bond was also carried out. We used a Si–H bond as an anchor to the metal center because it is well known that oxidative addition of a Si–H bond to a coordinatively unsaturated metal center proceeds readily and forms a thermally stable M–Si bond. As mentioned above, several types of μ -silicon ligands were obtained in the reactions of **1** with secondary silanes. In the reaction of **1** with dimethylvinylsilane, which has one Si–H bond and a vinyl group, coordination of both Si–H and C=C bonds to the ruthenium centers were observed as stated above, and it was shown that μ - η^2 : η^2 -coordination of vinylsilane would facilitate Si–C bond scission. When trimethylvinylsilane, which has no Si–H bond, was employed as a reactant, successive Si–C(sp²) and Si–C(sp³) bond cleavage occurred.

The reaction of **1** with 2.5 molar equiv of trimethylvinylsilane at 45 °C afforded μ -dimethylsilylene, μ -ethyldiyne complex (Cp*Ru)₂(μ -SiMe₂)(μ -CCH₃)(μ -H) (**8**) in 70% yield (eq 6). Small amounts of unidentified byproducts could be removed by rinsing with pentane to give analytically pure **8**.



When the reaction was carried out in a sealed tube at 0 °C, formation of trimethylethylsilane and methane was confirmed by means of ¹H NMR spectroscopy. While hydrogen was eliminated to form μ -vinylsilane complex **5a** in the reaction of dimethylvinylsilane, two hydrides were removed as trimethylethylsilane via hydrogenation of the vinyl group in this case. Though mechanistic details are not yet available at the present time, it can

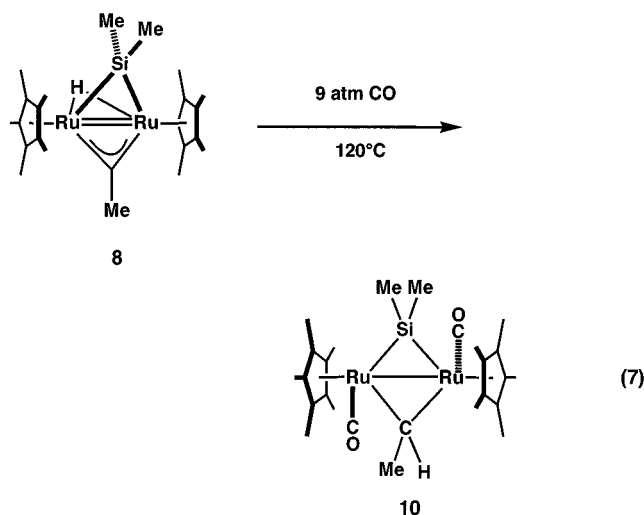
be said that two Si–C bonds were cleaved by the cooperative action of two rutheniums. This activation was assumed to be achieved via formation of a μ -trimethylvinylsilane intermediate as shown below. *Agostic* Si–C interaction was observed in a d_0 titanium complex $[\text{Cp}_2\text{Ti}\{\text{C}(\eta^2\text{-H}_3\text{C-SiMe}_2)=\text{CPhMe}\}]^+$, and this SiC \cdots Ti interaction was investigated theoretically by an *ab initio* MO method.^{23,24}



μ - η^2 : η^2 -Coordination of trimethylvinylsilane would result in the ready cleavage of the Si–C(sp^3) bond under such mild conditions. Si–C(sp^3) scission on the dinuclear system was also reported by Girolami et al.^{9c-e} The reaction of $\{\text{Cp}^*\text{Ru}(\mu\text{-Cl})\}_4$ with $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ resulted in formation of μ -methylidene complex $(\text{Cp}^*\text{Ru})_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\text{SiMe}_3)$ via formation of an intermediate trimethylsilylmethyl complex. This terminally bonded trimethylsilyl group, however, would not afford the μ -silylene ligand by further oxidative addition of the Si–C(sp^3) bond. It was assumed that a bridging chloride ligand decreases the electron density on the ruthenium centers so that oxidative addition of Si–C(sp^3) was suppressed. Conversely, formation of a μ -trimethylsilylmethyl group by reductive elimination between silyl and μ -methylidene occurred in the fluxional process of the complex.

Reaction of μ -Silylene, μ -Ethylidyne Complex **8 with Carbon Monoxide and Ethylene.** Due to the coordinatively unsaturated metal centers of **8** (32e) and its sterically less crowded ruthenium centers as revealed by X-ray studies, complex **8** readily reacts with some small molecules.

The reaction of complex **8** with 9 atm of CO at 120 °C yielded μ -silylene, μ -ethylidene complex $\{\text{Cp}^*\text{Ru}(\text{CO})\}_2(\mu\text{-SiMe}_2)(\mu\text{-CHMe})$ (**10**) (eq 7). Complex **10** was purified



by column chromatography on alumina and could be isolated in 47% yield. All of the spectral data are consistent with the μ -ethylidene structure. It was shown

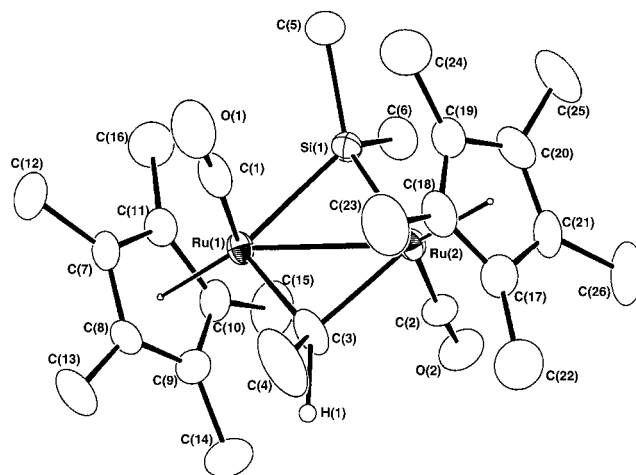


Figure 5. Molecular structure of $\{\text{Cp}^*\text{Ru}(\text{CO})\}_2(\mu\text{-SiMe}_2)(\mu\text{-CHMe})$ (**10**), with thermal ellipsoids at 30% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **10**

| | | | |
|------------------|-----------|------------------|----------|
| Ru(1)–Ru(2) | 2.8268(5) | Ru(1)–Si | 2.359(1) |
| Ru(2)–Si | 2.369(1) | Ru(1)–C(1) | 1.814(4) |
| Ru(1)–C(3) | 2.076(5) | Ru(2)–C(2) | 1.883(8) |
| Ru(2)–C(3) | 1.874(8) | Si–C(5) | 1.497(8) |
| Si–C(6) | 1.889(5) | C(1)–O(1) | 1.161(5) |
| C(2)–O(2) | 1.149(4) | C(3)–C(4) | 1.438(7) |
| Ru(2)–Ru(1)–Si | 53.45(4) | Ru(2)–Ru(1)–C(1) | 46.9(2) |
| Si–Ru(1)–C(3) | 103.0(2) | Ru(1)–Ru(2)–Si | 56.28(5) |
| Ru(1)–Ru(2)–C(3) | 46.3(2) | Si–Ru(2)–C(3) | 102.5(2) |
| Ru(1)–Si–Ru(2) | 67.53(6) | Ru(1)–Si–C(5) | 121.4(3) |
| Ru(1)–Si–C(6) | 120.1(3) | Ru(2)–Si–C(5) | 122.1(3) |
| Ru(2)–Si–C(6) | 120.3(3) | C(5)–Si–C(6) | 103.5(4) |
| Ru(1)–C(1)–O(1) | 176.0(4) | Ru(2)–C(2)–O(2) | 177.0(4) |
| Ru(1)–C(3)–Ru(2) | 86.8(2) | Ru(1)–C(3)–C(4) | 137.5(4) |
| Ru(2)–C(3)–C(4) | 135.7(5) | | |

that the hydride migration to the bridging carbon resulted in formation of the μ -ethylidene ligand.

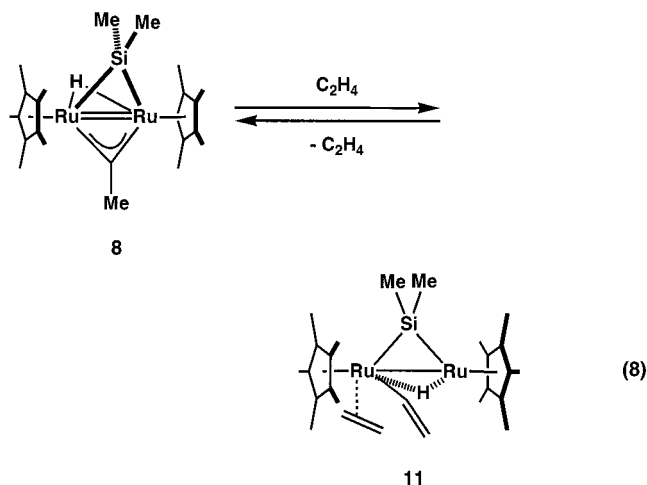
The μ -ethylidene carbon signal was observed at δ 142.7 (d, $J_{\text{C-H}} = 137.4$ Hz) in the ^{13}C NMR spectrum, which is characteristic for the alkylidene carbon. The ^{29}Si signal of the μ -silylene ligand was observed in the low-field region (δ 213.2). The ν_{CO} was observed at 1912 and 1899 cm^{-1} , which were assignable to ν_{sym} and ν_{asym} , respectively. The trans structure was confirmed by the fact that the intensity of ν_{asym} was stronger than that of ν_{sym} . The structure of complex **10** was determined by means of X-ray diffraction studies; the ORTEP diagram is shown in Figure 5, and selected bond lengths and angles are listed in Table 3.

While complex **8** did not react with propylene, it did react with 1 atm of ethylene at room temperature to yield μ -silylene, μ -vinyl complex $(\text{Cp}^*\text{Ru})_2(\mu\text{-SiMe}_2)(\mu\text{-}\eta^2\text{-CH=CH})(\mu\text{-H})(\text{CH}_2=\text{CH}_2)$ (**11**) as the sole product (eq 8). Complex **11** was characterized by means of ^1H , ^{13}C , and ^{29}Si NMR and ^1H – ^{13}C and ^{13}C – ^{13}C COSY.

In the ^1H NMR spectrum of **11**, the proton signals of the μ - η^2 -coordinated vinyl group were found at δ 1.69 (d, $J = 9.2$ Hz), δ 2.38 (d, $J = 6.4$ Hz), and δ 8.96 (dd, $J = 9.2, 6.4$ Hz). Such a low-field shift of the α -proton of the vinyl group is characteristic for the proton on the

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carbene carbon and strongly suggests μ - σ - π -coordination of the vinyl group. The ^{13}C signals of the vinyl group were found at δ 39.6 (t, $J_{\text{C-H}} = 157.7$ Hz) and δ 174.2 (d, $J_{\text{C-H}} = 154.8$ Hz), which also implied μ - σ - π -coordination. Signals of the π -coordinated ethylene were found at δ 1.00, 1.10, 1.50, and 1.60 in the ^1H NMR spectrum and δ 36.8 (t, $J_{\text{C-H}} = 155.5$ Hz) and δ 41.9 (t, $J_{\text{C-H}} = 156.2$ Hz) in the ^{13}C NMR spectrum. The μ -silylene coordination was confirmed by the ^{29}Si signal found at δ 205.7 (s).

Complex **11** slowly decomposed at 40 °C under an argon atmosphere and mainly regenerated complex **8** with a small amount of unidentified byproducts. Insertion of the coordinated ethylene into the Ru–Si bond was not observed.

When a π -acceptor coordinates to one ruthenium, the reductive elimination of hydride and μ -ethylidyne would be promoted and result in formation of the μ -ethylidene ligand. Carbon monoxide seems to be small enough to coordinate on the intermediate **A** in Scheme 3, so dicarbonyl complex **10** would be produced. On the other hand, ethylene is so large that coordination of the second ethylene is suppressed and β -H elimination to form the μ - σ - π -vinyl group takes place instead.

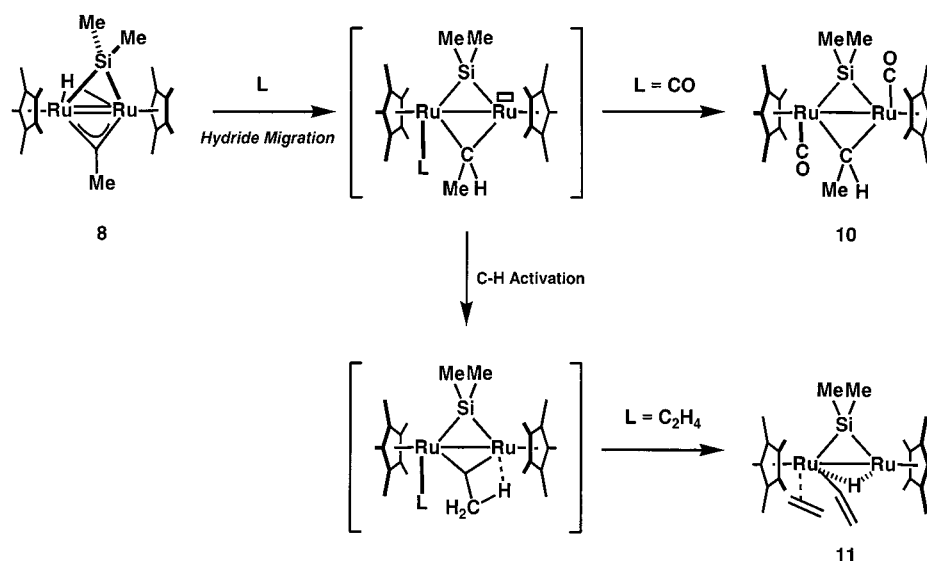
Reaction of μ -Silylene, μ -Ethylidyne Complex **8** with Molecular Hydrogen; Reductive Elimination

between Two Bridging Elements. When complex **8** was treated with 1 atm of hydrogen at room temperature, dinuclear tetrahydride complex **1** was generated. Complex **8** was completely consumed within 48 h. The dimethylsilylene and ethylidyne bridges were mainly eliminated as dimethylethylsilane, and the yield of dimethylethylsilane was estimated roughly at 30% by means of ^1H NMR spectroscopy. While a few unidentified organosilicon compounds were produced, there was no sign of formation of dimethylvinylsilane or dimethylsilane in the ^1H NMR spectrum.

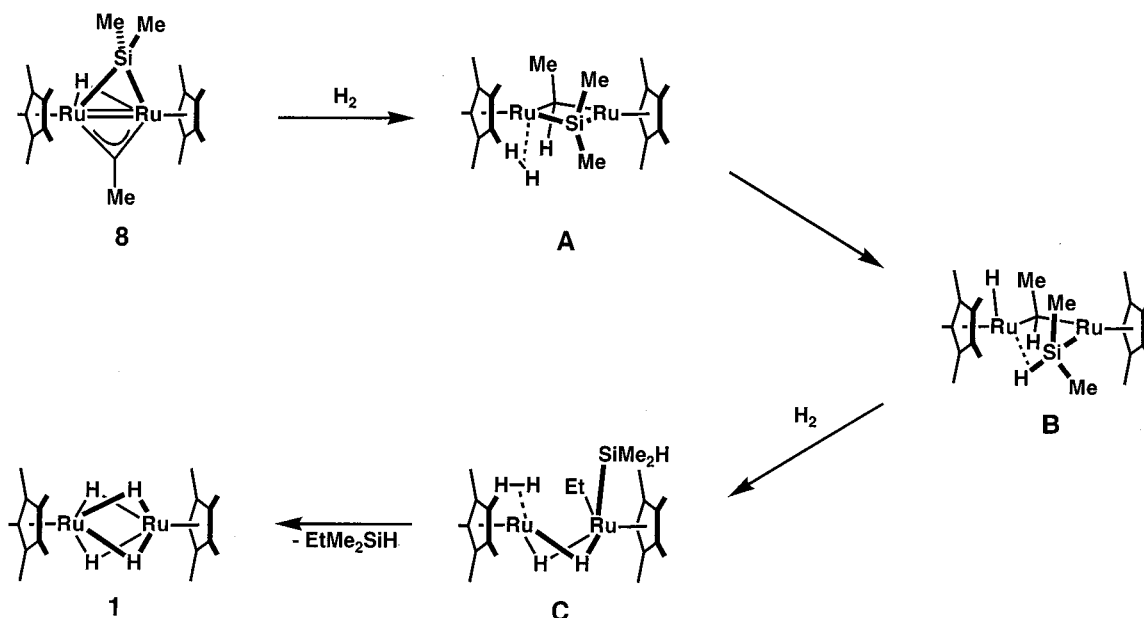
It was assumed that the reaction proceeded as shown in Scheme 4. Hydrogen coordinates on one ruthenium as a 2e donor; then hydride ligands migrate on the bridging ethylidyne ligand to form an intermediate similar to **A** of the reaction of carbon monoxide and ethylene. Coordination of the second hydrogen molecule and reduction of both bridging ligands would occur (intermediate **B**). Reductive elimination of dimethylethylsilane from the intermediacy silyl–alkyl complex **C** forms tetrahydride complex **1**. Re-formation of the μ -vinylsilane intermediate from **A** would be also possible by β -hydrogen elimination of the μ -ethylidene ligand. Sometimes vinylsilanes were detected as side-products of hydrosilylation, which implied the formation of vinylsilyl intermediates of the silyl-metalation path (i.e., olefin insertion into an M–Si bond).¹⁹ In this reaction, however, formation of neither vinylsilanes nor vinylsilane complexes was detected, and thus it supports the mechanism shown in Scheme 4.

While we previously showed a reaction of bis- μ -silylene complex **4** with acetylene to form 2,5-disilarythenacyclopentene complex $\{\text{Cp}^*\text{Ru}(\mu\text{-H})_2\}_2\{\mu\text{-}\eta^2\text{-SiPh}_2\text{C}(\text{H})=\text{C}(\text{H})\text{SiPh}_2\}$, in which Si–C coupling also occurred,⁴¹ this was a case of reductive Si–C bond formation on the dinuclear system. Girolami et al. showed reversible Si–C bond formation on the dinuclear complex $(\text{Cp}^*\text{Ru})_2(\mu\text{-Cl})(\mu\text{-CH}_2)(\text{SiR}_3)_2$ by means of a dynamic NMR study.^{9c–e} Akita et al. also showed Si–C coupling between a μ -methylene and a terminally bonded silyl group and reductive elimination of tetramethylsilane by thermolysis of $\{\text{CpRu}(\text{CO})\}_2(\mu\text{-CH}_2)(\mu\text{-CO})$ in the presence of trimethylsilane.^{9i,j,25} These reactions support the

Scheme 5



Scheme 6



reductive Si–C bond formation step from the intermediate **C** in Scheme 4. Although a number of complexes containing two bridging group 14 elements have been prepared, a coupling reaction between two bridging elements is still rare.²⁶ Especially, the coupling reaction including the μ -silylene ligand is quite limited.²⁷ Fryzuk et al. proposed a Si–C coupling reaction between μ -silyl and μ -alkyl ligands only in catalytic hydrosilylation using a dirhodium complex.²⁸ To the best of our knowledge, this is the first example of the reductive elimination between μ -silylene and another bridging element by using an isolated dinuclear complex.

Conclusion

The μ -vinylsilane complex $\{Cp^*Ru(\mu-H)_2\{\mu-\eta^2:\eta^2-HSiMe_2(CH=CH_2)\}\}$ (**5a**) was obtained by the reaction of $Cp^*Ru(\mu-H)_4RuCp^*$ (**1**) with dimethylvinylsilane. A unique $\mu-\eta^2:\eta^2$ -coordination of $HSiMe_2(CH=CH_2)$ was confirmed on the basis of 1H , ^{13}C , and ^{29}Si NMR and IR spectral and X-ray diffraction studies. Both Si–H and C=C bond coordination renders the Si–C(sp^2) bond subject to scission under mild conditions. This demonstrates that the Si–C(sp^2) bond was activated by multiple coordination. Thermolysis of **5a** yielded μ -silylene, μ -ethylidyne complex $(Cp^*Ru)_2(\mu-SiMe_2)(\mu-CCH_3)(\mu-H)$ (**8**) via formation of μ -silyl, μ -vinyl complex $(Cp^*Ru)_2(\mu-\eta^2-HSiMe_2)(\mu-CH=CH_2)(\mu-H)(H)$ (**9a**) as an intermediate.

The reaction of **1** with trimethylvinylsilane also yielded **8**, in which both Si–C(sp^2) and Si–C(sp^3) bonds were cleaved. The effect of two neighboring rutheniums

was also shown in this reaction. Oxidative addition of even an inert Si–C(sp^3) bond was achieved on the dinuclear system, which is a typical example of bimetallic activation.

Complex **8** obtained by the reaction of $Cp^*Ru(\mu-H)_4RuCp^*$ (**1**) with vinylsilanes is a novel type of complex that has both a silylene and an ethylidyne bridge in its structure. Coordinatively unsaturated metal centers of **8** led to easy reaction with 2e donors. Treatment of μ -silylene, μ -ethylidyne complex **8** with small 2e donors, CO and $CH_2=CH_2$, resulted in the transformation of the μ -ethylidyne ligand to the μ -ethylidene and μ -vinyl ligand, respectively. In the reaction of H_2 , elimination of both the μ -ethylidyne and μ -silylene bridge of **8** as dimethylethylsilane was observed, and complex **1** was regenerated. Reductive elimination of bridging ligands is a new type of reaction of dinuclear systems, and we are eager to investigate the further reactivity of **8** to build up dinuclear catalytic reaction systems using bimetallic activation.

Experimental Section

General Procedures. All experiments were carried out under an argon atmosphere. All compounds were treated with Schlenk techniques. Reagent grade toluene was dried over sodium-benzophenone ketyl and stored under an argon atmosphere. Pentane was dried over phosphorus pentoxide and stored under an argon atmosphere. Benzene- d_6 , toluene- d_8 , and THF- d_8 were dried over sodium-benzophenone ketyl and stored under an argon atmosphere. Dimethylvinylsilane and Dimethylvinylsilane- d were synthesized by the reduction of chlorodimethylvinylsilane by $LiAlH_4$ or $LiAlD_4$ in diglyme, respectively. (\pm)-Phenylmethylvinylsilane and (\pm)-phenylmethylvinylsilane- d were synthesized by the reduction of (\pm)-chlorophenylmethylvinylsilane by $LiAlH_4$ or $LiAlD_4$ in diethyl ether, respectively. Trimethylvinylsilane and other substrates were used as received. IR spectra were recorded on a JASCO FT/IR-5000 spectrophotometer. 1H and ^{13}C NMR spectra were recorded on JEOL GX-500, Varian Gemini-3000, and Varian INOVA-400 Fourier transform spectrometers with tetramethylsilane as an internal standard. Variable-temperature 1H NMR spectra were recorded on a Varian INOVA-400. ^{29}Si

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(28) (a) Fryzuk, M. D.; Piers, W. E.; Einstein, F. W. B.; Jones, T. *Can. J. Chem.* **1989**, 67, 883. (b) Fryzuk, M. D.; Rosenberg, L.; Rettig, S. J. *Organometallics* **1996**, 15, 2871. (c) Fryzuk, M. D.; Rosenberg, L.; Rettig, S. J. *Organometallics* **1991**, 10, 2537.

NMR spectra were recorded on a JEOL EX-270 and a Varian INOVA-400 with tetramethylsilane as an external standard. ^2H NMR spectra were recorded on a JEOL EX-270 and a Varian INOVA-400 with benzene- d_6 as an internal standard. Field-desorption mass spectra were recorded on a Hitachi GC-MS M80 high-resolution mass spectrometer. Coldspray ionization mass (CSI-MS)²⁹ spectra of a mixture of **5b/5b'** were recorded on a JEOL JMS-700T equipped with the CSI source at the Chemical Analysis Center at Chiba University. Elemental analyses were performed by the Analytical Facility at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology. The dinuclear ruthenium tetrahydride complex ($\eta^5\text{-C}_5\text{Me}_5$)Ru($\mu\text{-H}$)₄Ru($\eta^5\text{-C}_5\text{Me}_5$) (**1**) and ($\eta^5\text{-C}_5\text{Me}_5$)Ru($\mu\text{-D}$)₄-Ru($\eta^5\text{-C}_5\text{Me}_5$) (**1-d**) were prepared according to a previously published method.⁴

X-ray Data Collection and Reduction. X-ray-quality crystal of **5a**, **8**, and **10** were obtained directly from the preparations described below and mounted on glass fibers. Diffraction experiments were performed on a Rigaku AFC-5R four-circle diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å) at 23 °C. Intensity data were collected using a $\omega/2\theta$ scan technique; three standard reflections were recorded every 150 reflections. The data for **5a** and **10** were processed using the TEXSAN crystal solution package³⁰ operating on an IRIS Indigo computer, and the data for **8** were processed using the SHELX-97 programs.³¹ Neutral atom scattering factors were obtained from the standard sources.³² In the reduction of the data, Lorentz/polarization corrections and empirical adsorption corrections based on azimuthal scans were applied to the data for each structure.

Structure Solution and Refinement for 5a and 10. The Ru atom positions were determined using direct methods employing the MITHRIL-90³³ and SAPI-91³⁴ direct-methods routines for **5a** and **10**, respectively. In each case the remaining non-hydrogen atoms were located from successive difference Fourier map calculations using the DIRDIF-92 programs.³⁵ In both cases the non-hydrogen atoms were refined anisotropically by using full-matrix least-squares techniques on F . In the case of **5a**, the positions of hydrogen atoms bonded to the Ru were located by sequential difference Fourier synthesis and were refined isotropically. Crystal data and results of the analyses are listed in Table 4.

Structure Solution and Refinement for 8. The structure was solved by direct methods using SHELXS-97^{31a} and refined by full-matrix least-squares technique on F^2 with SHELXL-97.^{31b} The bridging silicon ligand, the methyl group of the μ -ethyldiyne ligand, and the hydride ligand of **8** were disordered over two sites related by a C_2 symmetry with 55.7 and 44.3% occupancy for each site, and the disordered atoms (C(1), C(2), C(3), C(4), Si(1), and H(1)) were refined isotropically. All hydrogen atoms were located by difference Fourier maps and refined isotropically, while all non-hydrogen atoms except for disordered atoms were refined anisotropically. Crystal data and results of the analyses are listed in Table 5.

Table 4. Crystallographic Data for **5a** and **10**

| | 5a | 10 |
|---|--|---|
| (a) Crystal Parameters | | |
| formula | C ₂₄ H ₄₂ Ru ₂ Si | C ₂₆ H ₄₀ O ₂ Ru ₂ Si |
| cryst syst | monoclinic | triclinic |
| space group | C_c | $P\bar{1}$ |
| a , Å | 10.458(1) | 9.826(3) |
| b , Å | 19.093(1) | 15.554(4) |
| c , Å | 13.474(1) | 9.698(3) |
| α , deg | | 96.08(2) |
| β , deg | 105.387(8) | 113.94(2) |
| γ , deg | | 91.97(2) |
| V , Å ³ | 1236.7(6) | 1342.2(6) |
| Z | 4 | 2 |
| D_{calcd} , g cm ⁻³ | 1.436 | 1.521 |
| temp, °C | 23 | 23 |
| $\mu(\text{Mo K}\alpha)$, cm ⁻¹ | 11.94 | 11.89 |
| cryst dims, mm | 0.10 × 0.15 × 0.30 | 0.10 × 0.20 × 0.20 |
| (b) Data Collection | | |
| diffractometer | Rigaku AFC-5R | Rigaku AFC-5R |
| radiation | Mo K α | Mo K α |
| | ($\lambda = 0.71069$ Å) | ($\lambda = 0.71069$ Å) |
| monochromator | graphite | graphite |
| scan type | $\omega/2\theta$ | $\omega/2\theta$ |
| $2\theta_{\text{max}}$, deg | 50.0 | 50.0 |
| scan speed, deg min ⁻¹ | 16.0 | 16.0 |
| no. of refls collected | 2493 | 5038 |
| no. of ind data | 2354 | 4735 |
| no. of ind data obsd | 2173 | 4069 |
| (c) Refinement | | |
| R | 0.022 | 0.029 |
| R_w ^b | 0.020 | 0.029 |
| p factor | 0.00 | 0.01 |
| no. of variables | 254 | 280 |
| GOF | 1.96 | 2.78 |

Variable-Temperature NMR Spectra and Dynamic NMR Simulations. Variable-temperature NMR studies were performed in flame-sealed NMR tubes in THF- d_8 /toluene- d_8 = 5:1 for **5a** and toluene- d_8 for **8** using a Varian INOVA-400 Fourier transform spectrometer with tetramethylsilane as an internal standard. NMR simulations for hydride ligands H^a (δ -9.28), H^b (δ -14.54), and H^c (δ -20.22) of **5** were performed using gNMR v4.1.0. (Ivory Soft, 1995–1999). The ^1H - ^1H coupling constants between them were estimated at 1.8 ($J_{\text{Ha-Hb}}$), 2.9 ($J_{\text{Ha-Hd}}$), and 3.9 ($J_{\text{Hb-Hd}}$) Hz from line shapes of signals. The $J_{\text{Si-H}}$ was estimated at 36.3 Hz from the line shape of satellite signals around H^a. Initial line widths (W) of these signals related to T_2 were estimated at 3.20 Hz (H^a), 2.55 Hz (H^b), and 2.82 Hz (H^c) from line widths of these signals at the lowest temperature. Final simulated line shapes were obtained via an iterative parameter search upon the exchange constant k . Full details of the fitting procedure may be found in the Supporting Information. The rate constants that accurately modeled the experimental spectra at each temperature are given in Figure 1. The activation parameters ΔH^\ddagger and ΔS^\ddagger were determined from the plot of $\ln(k/T)$ versus $1/T$. Estimated standard deviations (σ) in the slope and y -intercept of the Eyring plot determined the error in ΔH^\ddagger and ΔS^\ddagger , respectively. The standard deviation in ΔG^\ddagger was determined from the formula $\sigma(\Delta G^\ddagger)^2 = \sigma(\Delta H^\ddagger)^2 + [T\sigma(\Delta S^\ddagger)]^2 - 2T\sigma(\Delta H^\ddagger)\sigma(\Delta S^\ddagger)$.

Preparation of {Cp*Ru(μ -H)}₂{ μ - η^2 : η^2 -HSiMe₂(CH=CH₂)} (5a**).** Toluene (15 mL) and Cp*Ru(μ -H)₄RuCp* (0.229 g, 0.480 mmol) were charged in a reaction flask and cooled at -78 °C in a dry ice/methanol bath. After 2.5 equiv of dimethylvinylsilane (0.15 mL, 1.20 mmol) was added, the solution was gradually warmed to 5 °C with vigorous stirring. The reaction mixture was stirred for 7 h. The color of the solution changed from red to reddish-purple; 0.269 g of **5a** was obtained as a dark red solid on removal of the solvent and remaining silanes under reduced pressure (100% yield). A single crystal of **5a** was obtained from heptane solution at -20 °C. ^1H NMR (500 MHz, 23.0 °C, toluene- d_8): δ 4.50 (dd, $J_{\text{H-H}} = 11.0$, 2.0

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Table 5. Crystallographic Data for **8**

| (a) Crystal Parameters | | (b) Data Collection | |
|--|--|--------------------------------------|--|
| formula | C ₂₄ H ₄₀ Ru ₂ Si | diffractometer | Rigaku AFC-5R |
| cryst syst | triclinic | radiation | Mo K α (λ = 0.71069 Å) |
| space group | $P\bar{1}$ | monochromator | graphite |
| <i>a</i> , Å | 10.411(6) | scan type | $\omega/2\theta$ |
| <i>b</i> , Å | 14.072(5) | $2\theta_{\max}$, deg | 50.0 |
| <i>c</i> , Å | 10.015(5) | scan speed, deg min ⁻¹ | 16.0 |
| α , deg | 100.77(4) | no. of reflns measd | 4579 |
| β , deg | 117.82(4) | no. of ind reflns | 4321 |
| γ , deg | 71.52(4) | no. of reflns obsd [$I > 2\sigma$] | 3337 |
| <i>V</i> , Å ³ | 1229.5(11) | | |
| <i>Z</i> | 2 | | |
| (c) Refinement | | | |
| <i>D</i> _{calcd} , g cm ⁻³ | 1.509 | R1 [$I > 2\sigma$] | 0.0354 |
| temp, °C | 20 | wR2 [$I > 2\sigma$] | 0.0871 |
| μ (Mo K α), cm ⁻¹ | 12.84 | no. of params | 259 |
| cryst dimens, mm | 0.10 × 0.20 × 0.15 | GOF on <i>F</i> ² | 1.037 |

Hz, 1H, $-\text{CH}=\text{CH}_2$), 3.87 (dd, $J_{\text{H-H}} = 15.0$, 2.0 Hz, 1H, $-\text{CH}=\text{CH}_2$), 3.72 (dd, $J_{\text{H-H}} = 15.0$, 11.0 Hz, 1H, $-\text{CH}=\text{CH}_2$), 1.84 (s, 15H, Cp*), 1.48 (s, 15H, Cp*), 0.78 (s, 3H, Si-CH₃), 0.28 (s, 3H, Si-CH₃), -14.50 (br, $W_{1/2} = 1275$ Hz, 3H, Ru-H). ¹H NMR (400 MHz, -70.0 °C, toluene-*d*₈/THF-*d*₈ = 1:5): δ 4.38 (dd, $J_{\text{H-H}} = 8.2$, 3.4 Hz, 1H, $-\text{CH}=\text{CH}_2$), 3.49 (m, 1H, $-\text{CH}=\text{CH}_2$), 3.27 (m, 1H, $-\text{CH}=\text{CH}_2$), 1.86 (s, 15H, Cp*), 1.43 (s, 15H, Cp*), 0.45 (s, 3H, Si-CH₃), 0.04 (s, 3H, Si-CH₃), -9.28 (br, $J_{\text{Si-H}} = 36.3$ Hz, 1H, Ru-H-Si), -14.54 (br, 1H, Ru-H), -20.22 (br, 1H, Ru-H). ¹³C NMR (125 MHz, 23.0 °C, toluene-*d*₈): δ 92.1 (s, C₅Me₅), 85.2 (s, C₅Me₅), 68.0 (d, $J_{\text{C-H}} = 136.1$ Hz, $-\text{CH}=\text{CH}_2$), 62.7 (t, $J_{\text{C-H}} = 154.1$ Hz, $-\text{CH}=\text{CH}_2$), 12.5 (q, $J_{\text{C-H}} = 126.6$ Hz, C₅Me₅), 10.6 (q, $J_{\text{C-H}} = 126.4$ Hz, C₅Me₅), 10.5 (q, $J_{\text{C-H}} = 118.9$ Hz, Si-CH₃), 9.1 (q, $J_{\text{C-H}} = 114.6$ Hz, Si-CH₃). ²⁹Si NMR (79.5 MHz, 23.0 °C, THF-*d*₈): δ -8.0 (d, $J_{\text{Si-H}} = 31.0$ Hz). ²⁹Si NMR (79.5 MHz, -70.0 °C, THF-*d*₈): δ -8.6 (d, $J_{\text{Si-H}} = 54.1$ Hz). IR (KBr, cm⁻¹): 2961, 2902, 1943 ($\nu(\text{Ru-H-Si})$), 1541, 1526, 1477, 1452, 1377, 1313, 1222, 116, 1025, 832, 748. FD-MS: *m/z* 562. The field desorption mass spectrum was measured, and the intensities of the obtained isotopic peaks for C₂₄H₄₂Ru₂Si agreed with the calculated value within experimental error. Anal. Calcd for C₂₄H₄₂Ru₂Si: C, 51.40; H, 7.55. Found: C, 50.30; H, 6.98.

Preparation of {Cp*Ru(μ -H)}₂{ μ - η^2 : η^2 -HSiPhMe(CH=CH₂)} (5b** and **5b'**).** The same procedure as for **5a** was used for preparing a mixture of **5b** and **5b'** with 0.106 g of **1** (0.222 mmol) and 74 μ L of (\pm)-phenylmethylvinylsilane (0.445 mmol) in 10 mL of toluene; a 0.123 g of a red solid was obtained including two diastereomers, **5b** and **5b'**, on removal of the solvent under reduced pressure (90% yield). The ratio between **5b** and **5b'** was estimated as 56:44 by means of ¹H NMR spectroscopy. ¹H NMR (400 MHz, 30.0 °C, THF-*d*₈): (**5b**) δ 7.55 (m, 2H, Ph), 7.18 (m, 2H, Ph), 7.10 (m, 1H, Ph), 4.54 (dd, $J_{\text{H-H}} = 10.0$, 2.4 Hz, 1H, $-\text{CH}=\text{CH}_2$), 3.71 (dd, $J_{\text{H-H}} = 15.0$, 2.0 Hz, 1H, $-\text{CH}=\text{CH}_2$), 3.64 (dd, $J_{\text{H-H}} = 15.0$, 10.0 Hz, 1H, $-\text{CH}=\text{CH}_2$), 1.72 (s, 15H, Cp*), 1.59 (s, 15H, Cp*), 0.30 (s, 3H, Si-CH₃), -14.50 (br, $W_{1/2} = 1400$ Hz, 3H, Ru-H); (**5b'**) δ 7.33 (m, 2H, Ph), 7.06 (m, 2H, Ph), 6.99 (m, 1H, Ph), 4.47 (dd, $J_{\text{H-H}} = 9.2$, 2.8 Hz, 1H, $-\text{CH}=\text{CH}_2$), 3.46 (dd, $J_{\text{H-H}} = 15.0$, 2.8 Hz, 1H, $-\text{CH}=\text{CH}_2$), 3.39 (dd, $J_{\text{H-H}} = 15.0$, 9.2 Hz, 1H, $-\text{CH}=\text{CH}_2$), 1.70 (s, 15H, Cp*), 1.59 (s, 15H, Cp*), 0.68 (s, 3H, Si-CH₃), -14.50 (br, $W_{1/2} = 1400$ Hz, 3H, Ru-H). ¹H NMR (400 MHz, -70.0 °C, THF-*d*₈): (**5b**) δ 7.52 (m, 2H, Ph), 7.22 (m, 2H, Ph), 7.14 (m, 1H, Ph), 4.54 (dd, $J_{\text{H-H}} = 9.6$, 2.4 Hz, 1H, $-\text{CH}=\text{CH}_2$), 3.64 (m, 2H, $-\text{CH}=\text{CH}_2$ and $-\text{CH}=\text{CH}_2$), 1.69 (s, 15H, Cp*), 1.58 (s, 15H, Cp*), 0.28 (s, 3H, Si-CH₃), -9.15 (s, $J_{\text{Si-H}} = 38.0$ Hz, 1H, Ru-H-Si), -14.25 (m, 1H, Ru-H), -19.79 (m, 1H, Ru-H); (**5b'**) δ 7.31 (m, 2H, Ph), 7.10 (m, 2H, Ph), 7.03 (m, 1H, Ph), 4.43 (dd, $J_{\text{H-H}} = 8.8$, 2.8 Hz, 1H, $-\text{CH}=\text{CH}_2$), 3.32 (m, 2H, $-\text{CH}=\text{CH}_2$ and $-\text{CH}=\text{CH}_2$), 1.66 (s, 15H, Cp*), 1.61 (s, 15H, Cp*), 0.66 (s, 3H, Si-CH₃), -9.45 (s, $J_{\text{Si-H}} = 35.2$ Hz, 1H, Ru-H-Si), -14.21 (m, 1H, Ru-H), -20.20 (m, 1H, Ru-

H). ¹³C{¹H} NMR (100 MHz, 23.0 °C, benzene-*d*₆): (**5b**) δ 147.7 (*ipso*-C Ph), 135.0 (Ph), 127.4 (Ph), 127.2 (Ph), 92.7 (C₅Me₅), 85.37 (s, C₅Me₅), 70.4 ($-\text{CH}=\text{CH}_2$), 65.0 ($-\text{CH}=\text{CH}_2$), 12.1 (C₅Me₅), 10.7 (C₅Me₅), 7.2 (Si-CH₃). (**5b'**) δ 147.0 (*ipso*-C Ph), 134.9 (Ph), 126.7 (Ph), 126.6 (Ph), 92.8 (C₅Me₅), 85.36 (s, C₅Me₅), 66.2 ($-\text{CH}=\text{CH}_2$), 64.0 ($-\text{CH}=\text{CH}_2$), 12.0 (C₅Me₅), 10.8 (C₅Me₅), 6.4 (Si-CH₃). ²⁹Si NMR (79.5 MHz, 23.0 °C, benzene-*d*₆): (**5b**) δ -11.7 (d, $J_{\text{Si-H}} = 38.9$ Hz); (**5b'**) δ -2.9 (d, $J_{\text{Si-H}} = 39.0$ Hz). CSI-MS: *m/z* 622. The Coldspray ionization mass spectrum was measured, and the intensities of the obtained isotopic peaks for [C₂₉H₄₄Ru₂Si - 2H]⁺ agreed with the calculated value within experimental error.

Reaction of Cp*Ru(μ -D)₄RuCP* (1-d**) with HSiMe₂-(CH=CH₂).** Toluene (5 mL) and Cp*Ru(μ -D)₄RuCP* (10 mg, 0.021 mmol) were charged in a reaction flask and cooled at -78 °C in a dry ice/methanol bath. After 5 equiv of dimethylvinylsilane (13 μ L, 0.10 mmol) was added, the solution was gradually warmed to 5 °C with vigorous stirring. The reaction mixture was stirred for 18 h. After the solvent and excess silane were removed under reduced pressure, the residual solid was dissolved in toluene-*d*₈. ¹H NMR studies upon this solid reveal that the H/D ratio of the hydride region was 86:14. The reaction of **1** with 3.0 equiv of DSiMe₂(CH=CH₂) also afforded partially deuterated **5a**. The H/D ratio was estimated at 47:53 by means of ¹H NMR.

Reaction of DSiMe₂(CH=CH₂) with {Cp*Ru(μ -H)}₂{ μ - η^2 : η^2 -HSiPhMe(CH=CH₂)} (5b** and **5b'**).** A 20.3 mg sample of a mixture of {Cp*Ru(μ -H)}₂{ μ - η^2 : η^2 -HSiPhMe(CH=CH₂)} (**5b** and **5b'**; 0.033 mmol) was placed in a reaction flask and dissolved in 10 mL of toluene. The reaction flask was cooled at -78 °C in a dry ice/methanol bath; then 80 μ L of DSiMe₂-(CH=CH₂) (1.36 mmol) was added. The reaction mixture was vigorously stirred for 5 h at 5 °C. After the solvent and excess silane were removed under reduced pressure, the residual solid was dissolved in toluene-*d*₈. ¹H NMR studies of this solid reveal that 70% of the hydride ligands of **5b** and **5b'** were replaced by deuterium and no **5a** was produced.

Preparation of (Cp*Ru)₂(μ -SiMe₂)(μ -CCH₃)(μ -H) (8**).** Toluene (20 mL) and Cp*Ru(μ -H)₄RuCP* (0.546 g, 1.15 mmol) were charged in a reaction flask at 23 °C. After 2.5 equiv of trimethylvinylsilane (0.44 mL, 2.86 mmol) was added, the solution was gently heated at 45 °C with vigorous stirring for 24 h. The solvent and remaining silanes were removed under reduced pressure, and the residual solid was rinsed with 2 mL of pentane three times. Removal of pentane under reduced pressure afforded 0.478 g of **8** as a dark brown crystalline solid (71% yield). ¹H NMR (500 MHz, 10.0 °C, toluene-*d*₈): δ 3.95 (s, 3H, CCH₃), 1.76 (s, 30H, Cp*), 1.70 (br, 3H, Si-CH₃), 0.66 (br, 3H, Si-CH₃), -17.94 (s, 1H, Ru-H). ¹H NMR (500 MHz, -60.0 °C, toluene-*d*₈): δ 4.01 (s, 3H, CCH₃), 1.75 (s, 3H, Si-CH₃), 1.71 (s, 30H, Cp*), 0.75 (s, 3H, Si-CH₃), -17.78 (s, $J_{\text{Si-H}} = 22$ Hz, 1H, Ru-H). ¹³C NMR (125 MHz, -60.0 °C, toluene-

d_6): δ 387.7 (s, CCH_3), 91.8 (s, C_5Me_5), 40.0 (q, $J_{C-H} = 124.9$ Hz, CCH_3), 14.3 (q, $J_{C-H} = 119.1$ Hz, $Si-CH_3$), 13.1 (q, $J_{C-H} = 119.1$ Hz, $Si-CH_3$), 11.1 (q, $J_{C-H} = 126.6$ Hz C_5Me_5). ^{29}Si NMR (80 MHz, 23.0 °C, benzene- d_6): δ 197.8 (d, $J_{Si-H} = 22.7$ Hz). IR (KBr, cm^{-1}): 2908, 1930, 1736, 1667, 1551, 1450, 1379, 1261, 1027, 919. Anal. Calcd for $C_{24}H_{40}Ru_2Si$: C, 51.59; H, 7.22. Found: C, 51.18; H, 7.21. FD-MS: m/z 560. The field desorption mass spectrum was measured, and the intensities of the obtained isotopic peaks for $C_{24}H_{40}Ru_2Si$ agreed with the calculated value within experimental error.

Thermolysis of $\{Cp^*Ru(\mu-H)\}_2\{\mu-\eta^2:\eta^2-HSiMe_2(CH=CH_2)\}$ (5a). An NMR tube was charged with benzene- d_6 (0.3 mL) and $\{Cp^*Ru(\mu-H)\}_2\{\mu-\eta^2:\eta^2-HSiMe_2(CH=CH_2)\}$ (5a) (0.005 g, 0.009 mmol). The tube was sealed and then heated at 30 °C. The resonances assignable to $(Cp^*Ru)_2(\mu-\eta^2-HSiMe_2)(\mu-CH=CH_2)(\mu-H)(H)$ (9a) and $(Cp^*Ru)_2(\mu-SiMe_2)(\mu-CCH_3)(\mu-H)$ (8) gradually appeared. The conversion of 5a was 50% in 10 h, and the yields of 9a and 8 were estimated at 20 and 8% by means of 1H NMR at that point, respectively. The content of 9a was then decreased by prolonged heating at 30 °C. After 50 h, 5a and 9a disappeared, and 8 and other unidentified complexes were finally found. The yield of 8 was estimated at 50% by means of 1H NMR. When the tube was heated at 80 °C, 5a was completely consumed in 1 h. During this reaction generation of intermediate 9a could not be monitored. The yield of 8 was 90% at that condition. 1H NMR of 9a (300 MHz, 23.0 °C, benzene- d_6): δ 6.71 (dd, $J_{H-H} = 10.8$, 7.6 Hz, 1H, $-CH=CH_2$), 3.17 (dd, $J_{H-H} = 7.6$, 2.4 Hz, 1H, $-CH=CH_2$), 3.08 (dd, $J_{H-H} = 10.8$, 2.4 Hz, 1H, $-CH=CH_2$), 2.00 (s, 15H, Cp^*), 1.69 (s, 15H, Cp^*), 0.62 (s, 3H, $Si-CH_3$), 0.54 (s, 3H, $Si-CH_3$), -13.19 (s, 2H, $Ru-H$), -14.10 (s, 1H, $Ru-H$). ^{29}Si NMR of 9a (80 MHz, -70.0 °C, THF- d_6): δ 71.5 (d, $J_{Si-H} = 59.6$ Hz).

H/D Exchange Reaction of $(Cp^*Ru)_2(\mu-SiMe_2)(\mu-CCH_3)(\mu-H)$ (8) with Benzene- d_6 . Benzene- d_6 (0.3 mL) and $(Cp^*Ru)_2(\mu-SiMe_2)(\mu-CCH_3)(\mu-H)$ (8) (0.010 g, 0.018 mmol) were charged in an NMR tube. The tube was sealed and heated in an oil bath at 100 °C for 2 days. New signals of the methyl group of the μ -ethynylidene ligand assignable to isotopomers of 9a were observed at δ 4.00 (s, $\mu-CCH_3$), δ 3.97 (t, $J_{H-D} = 2.0$ Hz, $\mu-CCH_2D$), and δ 3.94 (br, $\mu-CCHD_2$), respectively. The intensity ratio of those signals was estimated at 4.6:3.6:1.0 by 1H NMR spectra measured after 48 h, which means $\mu-CCH_3:\mu-CCH_2D:\mu-CCHD_2 = 1.5:1.8:1.0$. At the same time, it was observed that the intensity of the residual proton signal of benzene- d_6 was increased. 2H NMR spectra showed that deuterium was incorporated into methyl groups of $\eta^5-C_5Me_5$ (δ 1.70), a methyl group of μ -ethynylidene (δ 3.96), and a hydride site (δ -17.87).

Preparation of $(Cp^*Ru)_2(\mu-\eta^2-HSi^tBu_2)(\mu-CH=CH_2)(\mu-H)(H)$ (9b). Toluene (10 mL) and $\{Cp^*Ru(\mu-H)\}_2\{\mu-\eta^2:\eta^2-HSi^tBu_2\}$ (3) (0.154 g, 0.25 mmol) were charged in a reaction flask at 23 °C. The solution was stirred under 1 atm of acetylene at ambient temperature for 4 days. The color of solution changed from purple to red. The solvent was removed under reduced pressure. After the products were dissolved in 15 mL of pentane, a small amount of black precipitate was removed by filtration. Removal of the solvent afforded 0.141 g of 9b as an orange solid (88% yield). 1H NMR (300 MHz, 23.0 °C, benzene- d_6): δ 6.77 (dd, $J_{H-H} = 11.2$, 8.0 Hz, 1H, $-CH=CH_2$), 3.89 (dd, $J_{H-H} = 11.2$, 2.1 Hz, 1H, $-CH=CH_2$), 3.03 (dd, $J_{H-H} = 8.0$, 2.1 Hz, 1H, $-CH=CH_2$), 1.98 (s, 15H, Cp^*), 1.60 (s, 15H, Cp^*), 1.34 (s, 9H, Si^tBu), 1.27 (s, 9H, Si^tBu), -13.17 (br, 1H, $Ru-H$), -14.56 (br, 1H, $Ru-H$), -14.83 (s, 1H, $J_{Si-H} = 59$ Hz, $Ru-H$). ^{13}C NMR (76 MHz, 23.0 °C, benzene- d_6): δ 153.8 (d, $J_{C-H} = 142.3$ Hz, $-CH=CH_2$), 95.3 (s, C_5Me_5), 89.6 (s, C_5Me_5), 58.4 (dd, $J_{C-H} = 161.5$, 145.5 Hz, $-CH=CH_2$), 32.8₃ (q, $J_{C-H} = 124.9$ Hz, CMe_3), 32.7₉ (q, $J_{C-H} = 124.9$ Hz, CMe_3), 27.5 (s, CMe_3), 26.8 (s, CMe_3), 12.1 (q, $J_{C-H} = 126.4$ Hz, C_5Me_5), 11.2 (q, $J_{C-H} = 126.9$ Hz, C_5Me_5). ^{29}Si NMR (54 MHz, 23.0 °C, benzene- d_6): δ 98.8 (d, $J_{Si-H} = 57.2$ Hz). IR (KBr, cm^{-1}): 2980, 2902, 2852, 2062 ($\nu(Ru-H)$), 1581 ($\nu(Ru-H-Si)$), 1477, 1454, 1377, 1026,

813. Anal. Calcd for $C_{20}H_{54}Ru_2Si$: C, 55.87; H, 8.44. Found: C, 55.83; H, 8.38.

Preparation of $\{Cp^*Ru(CO)\}_2(\mu-SiMe_2)(\mu-CHMe)$ (10). Toluene (10 mL) and $(Cp^*Ru)_2(\mu-SiMe_2)(\mu-CCH_3)(\mu-H)$ (8) (0.132 g, 0.23 mmol) were charged in a glass autoclave with 7 atm of carbon monoxide. The reaction vessel was heated at 90 °C with vigorous stirring for 19 h. The color of the solution changed to bright yellow. After the solvent was evaporated under reduced pressure, the yellow residual solid was dissolved in 4 mL of toluene and purified by column chromatography on neutral alumina (Merck Art. 1097) with pentane/toluene (10:1). A bright yellow fraction was collected, and from this the solvent was removed under reduced pressure; 0.065 g of 10 was obtained as a yellow solid (31% yield). 1H NMR (300 MHz, 23.0 °C, benzene- d_6): δ 7.74 (q, $J_{H-H} = 7.4$ Hz, 1H, $-CHCH_3$), 2.86 (d, $J_{H-H} = 7.4$ Hz, 1H, $-CHCH_3$), 1.78 (s, 15H, Cp^*), 1.71 (s, 15H, Cp^*), 1.12 (s, 3H, $Si-CH_3$), 1.01 (s, 3H, $Si-CH_3$). ^{13}C NMR (68 MHz, 23.0 °C, benzene- d_6): δ 205.5 (s, CO), 203.8 (s, CO), 142.7 (d, $J_{C-H} = 137.4$ Hz, $-CHCH_3$), 98.6 (s, C_5Me_5), 97.7 (s, C_5Me_5), 37.9 (q, $J_{C-H} = 124.1$, $-CHCH_3$), 12.2 (q, $J_{C-H} = 120.1$ Hz, $Si-CH_3$), 11.9 (q, $J_{C-H} = 116.9$ Hz, $Si-CH_3$), 10.9 (q, $J_{C-H} = 127.0$ Hz, C_5Me_5), 10.2 (q, $J_{C-H} = 126.6$ Hz, C_5Me_5). ^{29}Si NMR (54 MHz, 23.0 °C, benzene- d_6): δ 213.2 (s). IR (KBr, cm^{-1}): 2896, 2436, 1912 ($\nu_{sym}(CO)$), 1899 ($\nu_{asym}(CO)$), 1481, 1379, 1288, 1234, 1015, 843, 764. Anal. Calcd for $C_{26}H_{40}O_2Ru_2Si$: C, 50.79; H, 6.56. Found: C, 50.61; H, 6.70. FD-MS: m/z 616. The field desorption mass spectrum was measured, and the intensities of the obtained isotopic peaks for $C_{26}H_{40}O_2Ru_2Si$ agreed with the calculated value within experimental error.

Preparation of $(Cp^*Ru)_2(\mu-SiMe_2)(\mu-\eta^2-CH=CH_2)(\mu-H)(CH_2=CH_2)$ (11). Toluene (10 mL) and $(Cp^*Ru)_2(\mu-SiMe_2)(\mu-CCH_3)(\mu-H)$ (8) (0.390 g, 0.70 mmol) were charged in a reaction flask. The solution was stirred under 1 atm of ethylene for 5 h at ambient temperature. The color of the solution changed from dark brown to orange. After the solvent was evaporated under reduced pressure, 0.046 g of brown residual solid was obtained. The content of 11 was estimated at 90% by 1H NMR analysis. Correlation between $^1H-^1H$ and $^1H-^{13}C$ of coordinate ethylene and the vinyl group of 11 was confirmed by means of $^1H-^1H$ COSY and $^1H-^{13}C$ COSY. 1H NMR (300 MHz, 23.0 °C, benzene- d_6): δ 8.96 (dd, $J_{H-H} = 9.2$, 6.4 Hz, 1H, $-CH=CH_2$), 2.38 (d, $J_{H-H} = 6.4$ Hz, 1H, $-CH=CH_2$), 1.69 (d, $J_{H-H} = 9.2$ Hz, 1H, $-CH=CH_2$), 1.65 (s, 15H, Cp^*), 1.60 (m, 1H, C_2H_4), 1.50 (m, 1H, C_2H_4), 1.48 (s, 15H, Cp^*), 1.18 (s, 3H, $Si-CH_3$), 1.15 (s, 3H, $Si-CH_3$), 1.10 (m, 1H, C_2H_4), 1.00 (m, 1H, C_2H_4), -11.85 (s, 1H, $Ru-H$). ^{13}C NMR (68 MHz, 23.0 °C, benzene- d_6): δ 174.2 (d, $J_{C-H} = 154.8$ Hz, $-CH=CH_2$), 93.2 (s, C_5Me_5), 92.9 (s, C_5Me_5), 41.9 (t, $J_{C-H} = 156.2$, C_2H_4), 39.6 (t, $J_{C-H} = 157.7$, $-CH=CH_2$), 36.8 (t, $J_{C-H} = 155.5$, C_2H_4), 18.5 (q, $J_{C-H} = 123.5$ Hz, $Si-CH_3$), 11.9 (q, $J_{C-H} = 120.9$ Hz, $Si-CH_3$), 10.9 (q, $J_{C-H} = 126.4$ Hz, C_5Me_5), 9.9 (q, $J_{C-H} = 126.7$ Hz, C_5Me_5). ^{29}Si NMR (54 MHz, 23.0 °C, benzene- d_6): δ 205.7 (s).

Reaction of $(Cp^*Ru)_2(\mu-SiMe_2)(\mu-CCH_3)(\mu-H)$ (8) with H_2 . An NMR tube equipped with a Roto Tite valve was charged with benzene- d_6 (0.3 mL) and $(Cp^*Ru)_2(\mu-SiMe_2)(\mu-CCH_3)(\mu-H)$ (8) (0.005 g, 0.009 mmol). The tube was degassed and then charged with 1 atm of hydrogen and kept at 25 °C. The progress of the reaction was monitored by means of 1H NMR. The resonance assignable to $Cp^*Ru(\mu-H)_4RuCp^*$ (1) and dimethylethylsilane gradually appeared. The conversion of 8 to 1 was 20% in 3 h, and it took 48 h to consume all of 8. Owing to its low boiling temperature, the yield of dimethylethylsilane as estimated by means of 1H NMR spectra seemed not to be accurate, but the yield was roughly estimated at 30%. Generation of dimethylethylsilane was confirmed by the observation of 1H NMR signals as follows, and correlation between each signal was confirmed by the decoupling experiments (400 MHz, 23.0 °C, benzene- d_6): δ 4.07 (triplet of septet, $J_{H-H} = 3.0$, 2.8

Hz, 1H, SiH), 0.93 (t, $J_{H-H} = 8.1$ Hz, 3H, CH_2CH_3), 0.48 (dq, $J_{H-H} = 8.1, 2.8$ Hz, 2H, CH_2CH_3), 0.01 (d, $J_{H-H} = 3.0$ Hz, 6H, SiCH_3).

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Supporting Information Available: Tables of atomic coordinates and thermal parameters, bond lengths and angles, torsion angles, and structure refinement details and ORTEP drawing of **5a**, **8**, and **10** with full numbering schemes. Parameters for the dynamic NMR simulations of **5a**, **5b**, and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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