*Organometallics* **2005,** *24,* 521−532

# Substitution Reactions at a Bridging Silicon Ligand. Formation of a Bis($\mu$-silylene) Complex Containing a Trifluoroacetoxy Group. Mechanistic Studies of the Site-Exchange Process of the Hydride Ligands

Toshiro Takao, Shigeru Yoshida, and Hiroharu Suzuki*

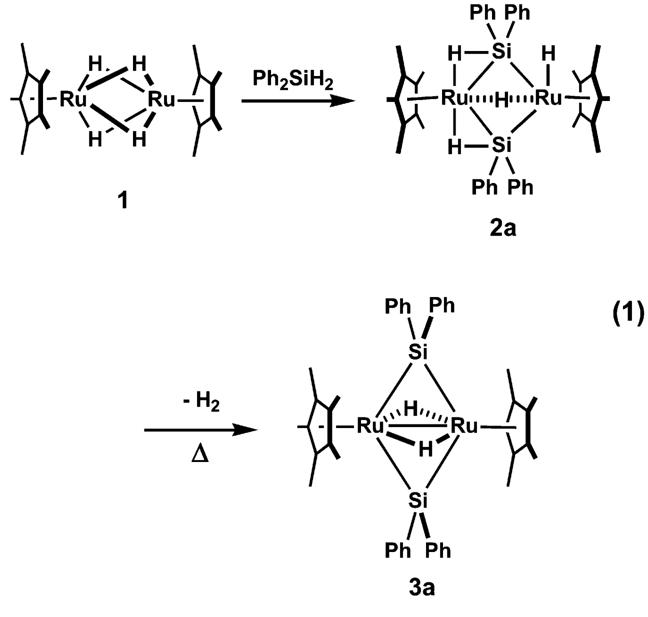
*Department of Applied Chemistry, Graduate School of Science and Engineering,*
*Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-Ku, Tokyo 152-8552, Japan*

*Received August 30, 2004*

Treatment of a bis($\mu$-diphenylsilyl) complex, $\{Cp^*Ru(\mu\text{-}\eta^2\text{-}HSiPh_2)\}_2(\mu\text{-}H)(H)$ (**2a**, Cp* = $\eta^5$-$C_5Me_5$), with trifluoroacetic acid in toluene resulted in introduction of a trifluoroacetoxy group on a bridging silicon atom with concomitant loss of one phenyl group as benzene, affording a mixed-bridging bis($\mu$-silylene) complex, $\{Cp^*Ru(\mu\text{-}H)\}_2\{\mu\text{-}SiPh(OCOCF_3)\}(\mu\text{-}SiPh_2)$ (**3b**), in moderate yield. Nucleophilic addition of the acetoxy group took place in the intermediate $\mu$-silyl,$\mu$-silylene complex $(Cp^*Ru)_2(\mu\text{-}\eta^2\text{-}HSiPh_2)(\mu\text{-}SiPh_2)(\mu\text{-}CF_3CO_2)(\mu\text{-}H)(H)$ (**7**), containing a bridging carboxylate group. The trifluoroacetoxy group of **3b** underwent nucleophilic displacement at the bridging silicon atom, which afforded the mixed-bridging bis($\mu$-silylene) complexes $\{Cp^*Ru(\mu\text{-}H)\}_2(\mu\text{-}SiPhX)(\mu\text{-}SiPh_2)$ (**3c**, X = OMe; **3d**, X = OH) upon treatment with methanol and aqueous KOH, respectively. VT NMR studies of **3b**, **3c**, **3d**, $\{Cp^*Ru(\mu\text{-}H)\}_2(\mu\text{-}SiPhMe)(\mu\text{-}SiMe_2)$ (**3e**), and $\{Cp^*Ru(\mu\text{-}H)(\mu\text{-}SiPhMe)\}_2$ (**3f-*syn***) revealed a linear correlation between the electronic nature of the substituents on the bridging silicon atom and the activation parameters of the hydride site-exchange process occurring in the bis($\mu$-silylene) complex.

## Introduction

We have studied the reactivity of the diruthenium tetrahydride complex $Cp^*Ru(\mu\text{-}H)_4RuCp^*$ (**1**, Cp* = $\eta^5$-$C_5Me_5$) with hydrosilanes in relation to bimetallic activation on the $Ru_2$ system.[1] We have shown that the reaction of **1** with diphenylsilane afforded the bis($\mu$-diphenylsilyl) complex $\{Cp^*Ru(\mu\text{-}\eta^2\text{-}HSiPh_2)\}_2(\mu\text{-}H)(H)$ (**2a**), whose 3c-2e Ru−H−Si bonds were readily cleaved upon thermolysis to yield the bis($\mu$-diphenylsilylene) complex $\{Cp^*Ru(\mu\text{-}SiPh_2)(\mu\text{-}H)\}_2$ (**3a**) (eq 1).[1a] This successive bond cleavage performed on the bimetallic system showed that the *agostic* Si−H interaction was really an intermediary state for the oxidative addition, and two metal nuclei played an important role during the bimetallic activation as a coordination site and an activation site.



(1)

Recently, we have demonstrated that protonation of the bis($\mu$-silyl) complexes in dichloromethane affords the cationic bis($\mu$-silane) complexes $[\{Cp^*Ru(\mu\text{-}\eta^2\text{:}\eta^2\text{-}H_2\text{-}SiR_2)\}_2(\mu\text{-}H)][X^-]$ (**4a**, R = Ph; **4b**, R = Et, X = $CF_3SO_3$, $BPh_4$) (eq 2).[2] The positive charge on the metal center caused reductive coupling between the bridging silyl ligand and the hydride, thereby resulting in transfor-

---

[1] (a) Suzuki, H.; Takao, T.; Tanaka, M.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 476−478. (b) Takao, T.; Yoshida, S.; Suzuki, H.; Tanaka, M. *Organometallics* **1995**, *14*, 3855−3868. (c) Takao, T.; Amako, M.; Suzuki, H. *Organometallics* **2001**, *20*, 3406−3422. (d) Takao, T.; Amako, M.; Suzuki, H. *Organometallics* **2003**, *22*, 3855−3876.

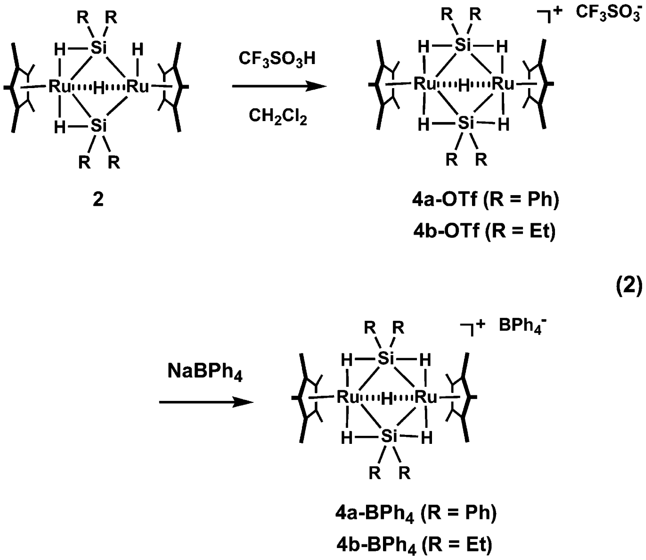
[2] Takao, T.; Yoshida, S.; Suzuki, H. *Chem. Lett.* **2001**, 1100−1101.

[3] See for example: (a) Davies, D. L.; Gracey, B. P.; Guerchais, V.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1984**, 841−843. (b) Herrmann, W. A.; Plank, J.; Riedel, D.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *J. Am. Chem. Soc.* **1981**, *103*, 53−75. (c) Gao, Y.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2001**, *20*, 1882−1888. (d) Bower, D. K.; Keister, J. B. *J. Organomet. Chem.* **1986**, *312*, C33−C36. (e) Bower, D. K.; Keister, J. B. *Organometallics* **1990**, *9*, 2321−2327. (f) Casey, C. P.; Fagan, P. J.; Miles, W. H.; Marder, S. R. *J. Mol. Catal.* **1983**, *21*, 173−188. (g) Calvert, R. B. Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726−7727.

[4] (a) Lemke, F. R. *J. Am. Chem. Soc.* **1994**, *116*, 11183−11184. (b) Freeman, S. T. N.; Lemke, F. R.; Brammer, L. *Organometallics* **2002**, *21*, 2030−2032. (c) Scharrer, E.; Chang, S.; Brookhart, M. *Organometallics* **1995**, *14*, 5686−5694.

[5] (a) Suzuki, H.; Kakigano, T.; Igarashi, M.; Tanaka, M.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 283−285. (b) Suzuki, H.; Kakigano, K.; Tada, K.; Igarashi, M.; Matsubara, K.; Inagaki, A.; Ohshima, M.; Takao, T. *Bull. Chem. Soc., Jpn.* **2005**, *78*, 1−21.

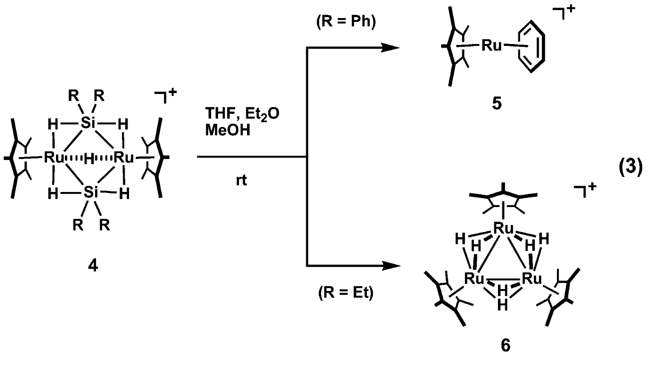
10.1021/om049328h CCC: $30.25



(2)

mation of the $\mu$-silyl ligand to the $\mu$-silane ligand. Although formation of an *agostic* M−H−C bond by protonation has been well documented for $\mu$-alkylidene and $\mu_3$-alkylidyne complexes,[3] formation of a cationic $\mu$-silane complex by protonation is still rare. Only limited examples of the protonation of a monometallic silyl complex to yield a cationic silane complex have been reported.[4]

We employed dichloromethane as solvent for the protonation. However, when other solvents, such as THF, $Et_2O$, and MeOH, were used, elimination of the silicon ligands resulted due to rapid nucleophilic attack at the electrophilic silicon center of the cationic $\mu$-silane complex. Protonation of **2a** and **2b** in $Et_2O$ led to the formation of the cationic $\eta^6$-benzene complex $[Cp^*Ru(\eta^6\text{-}C_6H_6)]^+$ (**5**) and the cationic triruthenium hexahydride complex $[Cp^*Ru(\mu\text{-}H)_2]_3^+$ (**6**),[5] respectively. Treatment of **4** with these solvents also gave the same result (eq 3). These facts implied formation of a monometallic $[Cp^*RuH_2]^+$ fragment via in situ elimination of the bridging silicon ligands. Especially, formation of **5** indicated generation of benzene as a result of Si−C(aryl) bond cleavage by protonation. Such instability toward nucleophiles has been well documented in the literature.[4] For example, $Et_3SiF$ was obtained in the reaction of $(C_5H_5)Fe(CO)(PEt_3)SiEt_3$ with $HBF_4$ as a result of nucleophilic attack of the $BF_4$ anion at the Fe-SiEt$_3$ group.[4c] Instability of **4** toward nucleophiles prompted us to investigate the reactivity of **4** with nucleophiles in a substitution reaction at the bridging silicon ligand.



(3)

Substitution reaction at an Si−H or Si−X bond on a bridging silylene ligand has been well investigated.[6] However, there are few example of the Si−C bond cleavage of an organic substituent on a bridging silyl group to introduce a functional group on silicon. Recently, bromodemethylation of the trimethylsilyl group attached to an iron center using $BBr_3$ was reported by Tobita and co-workers.[7] Herein, we report displacement of a phenyl group from a bridging silicon atom of the cationic bis($\mu$-silane) complex **4a** by trifluoroacetate ion to afford the neutral bis($\mu$-silylene) complex $\{Cp^*Ru(\mu\text{-}H)\}_2\{\mu\text{-}SiPh(OCOCF_3)\}(\mu\text{-}SiPh_2)$ (**3b**), having a trifluoroacetoxy group on the bridging silylene ligand. The trifluoroacetoxy group on the bridging silicon atom readily underwent nucleophilic displacement. Thus, complex **3b** could be a good precursor affording various mixed-bridging bis($\mu$-silylene) complexes.

In our preceding paper,[1d] we showed that the site-exchange process of the hydride ligands occurs in the bis($\mu$-silylene) complex **3**. This process occurs via the formation of an intermediate silyl complex containing an Si−H bond. Therefore, the energy level of the $\sigma^*$(Si−H) would affect the activation parameters of the fluxional process. The electronic nature of the substituents on the silicon atom has been shown to highly affect the energy level of the $\sigma^*$(Si−H) orbital.[8] Thus, kinetic studies of the bis($\mu$-silylene) complexes containing various substituents afford a deeper understanding of the fluxional process of the bis($\mu$-silylene) complex as well as the nature of the bridging silylene ligand.

## Results and Discussion

While the reaction of bis($\mu$-diphenylsilyl) complex **2a** with $CF_3SO_3H$ in $CH_2Cl_2$ quantitatively affords the cationic bis($\mu$-diphenylsilane) complex **4a** as shown eq 2,[2] the mixed-bridging bis($\mu$-silylene) complex $\{Cp^*Ru(\mu\text{-}H)\}_2\{\mu\text{-}SiPh(OCOCF_3)\}(\mu\text{-}SiPh_2)$ (**3b**) was obtained by the reaction of **2a** with trifluoroacetic acid in toluene (eq 4). Formation of **3b** was confirmed on the basis of $^1H$, $^{13}C$, and $^{29}Si$ NMR and IR spectra, respectively, as well as elemental analysis.

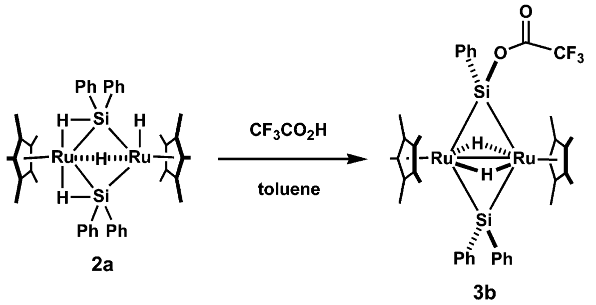
Introduction of the trifluoroacetoxy group at the bridging silicon atom was clearly shown in the $^{29}Si$ NMR spectra. While one signal appeared at $\delta$ 109.8 in the $^{29}Si$ NMR spectrum of the bis($\mu$-diphenylsilylene) complex **3a**, two signals were observed for **3b** at $\delta$ 109.2 and 137.5, respectively. The signal observed at $\delta$ 109.2 was straightforwardly assigned to the $\mu$-SiPh$_2$ bridge from its similarity of the chemical shift in **3a**. The signal observed at $\delta$ 137.5 is thus attributed to the $\mu$-SiPh(OCOCF$_3$) bridge.

---

(6) (a) Kawano, Y.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1994**, *116*, 8575−8581. (b) Kawano, Y.; Tobita, H.; Ogino, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 843−844. (c) Tobita, H.; Kawano, Y.; Ogino. H. *Chem. Lett.* **1989**, 2155−2158. (d) Malisch, W.; Ries, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 120−121. (e) Malish, W.; Ries, W. *Chem. Ber.* **1979**, *112*, 1304−1315. (f) Malisch, W.; Vögler, M.; Schumacher, D.; Nieger, M. *Organometallics* **2002**, *21*, 2891−2897. (g) Aylett, B. J.; Colquhoun, H. M. *J. Chem. Res., Synop.* **1977**, 148.

(7) Watanabe, T.; Hashimoto, H.; Tobita, H. *Organometallics* **2004**, *23*, 4150−4153.

(8) (a) Lichtenberger, D. L.; Rai-Chaudhuri, A. *J. Am. Chem. Soc.* **1989**, *111*, 3583−3591. (b) Lichtenberger, D. L.; Rai-Chaudhuri, A. *Inorg. Chem.* **1990**, *29*, 975−981. (c) Lichtenberger, D. L.; Rai-Chaudhuri, A. *Organometallics* **1990**, *9*, 1686−1690. (d) Lichtenberger, D. L.; Rai-Chaudhuri, A. *J. Am. Chem. Soc.* **1990**, *112*, 2492−2497.

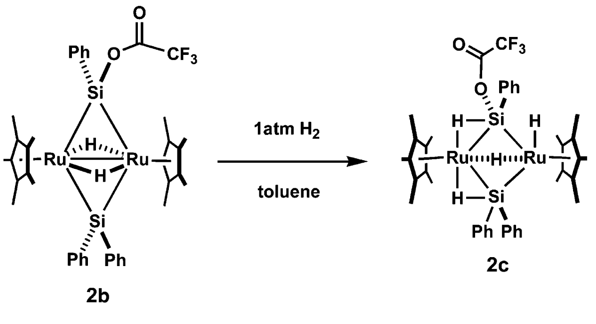


(4)

The magnetic environments of the hydride ligands of **3b** should be inequivalent because of the trifluoroacetoxy group on the bridging silicon atom. Nevertheless, only one signal was observed in the hydride region of the $^{1}$H NMR spectra measured at 21 °C. This means that site-exchange of the hydride ligands is occurring. Such motion of the hydride ligands of the bis($\mu$-silylene) complexes has been reported earlier in our previous paper.[1d] At $-65$ °C, the signal split into two sharp doublets at $\delta$ $-20.17$ and $-18.50$. These coalesced at 10 °C, and activation parameters were estimated as $\Delta H^{\ddagger} = 12.8 \pm 0.4$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = 1.9 \pm 1.5$ cal mol$^{-1}$ K$^{-1}$ by means of line shape analysis. Mechanistic studies of the fluxional processes are discussed in detail later.

In the IR spectra of **3b**, $\nu$(C=O) and $\nu$(C−F) of the trifluoroacetoxy group was observed at 1754 and 1164 cm$^{-1}$, respectively. In the $^{13}$C NMR spectra, two quartets coupled with the $^{19}$F nucleus were observed at $\delta$ 155.8 (q, $^{2}J_{\mathrm{C-F}} = 40.2$ Hz) and 115.9 (q, $J_{\mathrm{C-F}} = 288.0$ Hz), which were assignable to the carbonyl and $CF_3$ carbon atoms, respectively.

Although a single-crystal of **3b** suitable for the X-ray diffraction studies was not obtained, the trifluoroacetoxy group on the bridging silicon atom was confirmed by the X-ray diffraction studies of a bis($\mu$-silyl) complex, $(Cp^{*}Ru)_2(\mu\text{-}\eta^{2}\text{-}HSiPh_2)\{\mu\text{-}\eta^{2}\text{-}HSiPh(OCOCF_3)\}(\mu\text{-}H)(H)$ (**2c**), which was obtained by the reaction of **3b** with hydrogen (eq 5). Quantitative formation of a bis($\mu$-silyl) complex by hydrogenation is characteristic of the bis($\mu$-silylene) complexes.[1d]



(5)

The structure of **2c** is shown in Figure 1, and selected bond distances and angles are summarized in Table 1. The $Ru_2Si_2$ core of **2c** forms a folded quadrangle. The 3c-2e Ru−H−Si interactions were held on the adjacent two edges (Ru(2)−Si(1) and Ru(2)−Si(2)) as well as other bis($\mu$-silyl) complexes of the type $\{Cp^{*}Ru(\mu\text{-}\eta^{2}\text{-}HSiR_2)\}_2(\mu\text{-}H)(H)$ (**2**) synthesized by ourselves.[1a,b] It is in sharp contrast to other bimetallic bis($\mu$-silyl) complexes of rhodium,[9] platinum,[10] palladium,[11] and other transition metals,[12] in which two 3c-2e M−H−Si bonds were held on the edges opposite of each other and formed a $C_2$ structure. Two of the four hydride ligands, H(1) and H(2), are located between Ru(2) and the silicon atoms and form 3c-2e Ru−H−Si bonds. H(3) bridges Ru(1) and Ru(2), and the H(4) is coordinated to Ru(1) as a terminal hydride. Bond distances between Ru(2) and the silicon atoms were considerably longer than those between the Ru(1) and silicon atoms due to 3c-2e interaction (Ru(2)−Si(1), 2.4942(10) Å; Ru(1)−Si(1), 2.4223(11) Å; Ru(2)−Si(2), 2.4120(10) Å; Ru(1)−Si(2), 2.3395(10) Å). This structural difference between two ruthenium atoms was also confirmed by the $^{1}$H NMR spectra recorded at $-80$ °C, in which two Cp* signals and four hydride signals were observed. This fact indicates that the folded structure was also adopted in solution.

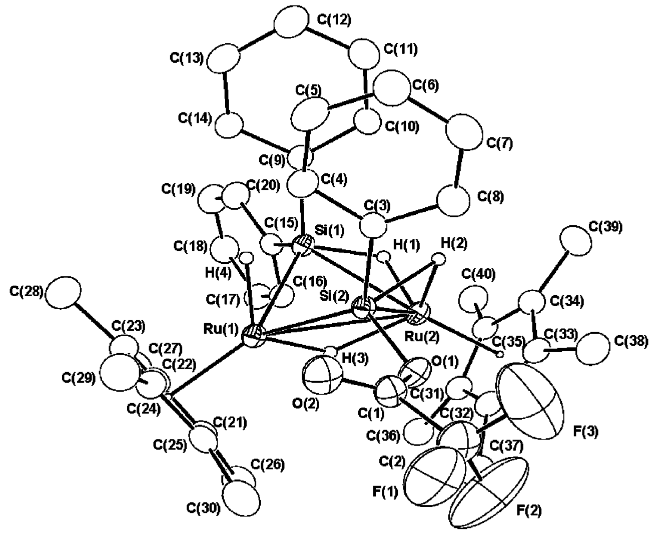


**Figure 1.** Molecular structure of $(Cp^{*}Ru)_2(\mu\text{-}\eta^{2}\text{-}HSiPh_2)\{\mu\text{-}\eta^{2}\text{-}HSiPh(OCOCF_3)\}(\mu\text{-}H)(H)$ (**2c**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms except for those attached to the ruthenium atoms were omitted for clarity.

**Table 1. Selected Bond Distances (Å) and Angles (deg) for 2c**

| | | | |
|---|---|---|---|
| Ru(1)−Ru(2) | 2.9878(7) | Ru(1)−Si(1) | 2.4223(11) |
| Ru(1)−Si(2) | 2.3395(10) | Ru(2)- Si(1) | 2.4942(10) |
| Ru(2)- Si(2) | 2.4120(10) | Si(1)−C(9) | 1.899(4) |
| Si(1)−C(15) | 1.888(4) | Si(2)−O(1) | 1.760(3) |
| Si(2)−C(3) | 1.891(4) | O(1)−C(1) | 1.291(5) |
| O(2)−C(1) | 1.203(5) | C(1)−C(2) | 1.512(6) |
| Ru(2)−Ru(1)−Si(1) | 53.68(3) | Ru(2)−Ru(1)−Si(2) | 52.13(2) |
| Si(1)−Ru(1)−Si(2) | 82.31(4) | Ru(1)−Ru(2)−Si(1) | 51.49(2) |
| Ru(1)−Ru(2)−Si(2) | 49.97(2) | Si(1)−Ru(2)−Si(2) | 79.39(3) |
| C(9)−Si(1)−C(15) | 107.76(16) | O(1)−Si(2)−C(3) | 99.57(15) |
| Si(2)−O(1)−C(1) | 122.2(3) | O(1)−C(1)−O(2) | 128.9(4) |
| O(1)−C(1)−C(2) | 112.3(4) | O(2)−C(1)−C(2) | 118.8(4) |

---

(9) (a) Fryzuk, M. D.; Rosenberg, L.; Rettig, S. J. *Inorg. Chim. Acta* **1994**, *222*, 345−364. (b) Fryzuk, M. D.; Rosenberg, L.; Rettig, S. J. *Organometallics* **1999**, *18*, 958−969.

(10) (a) Auburn, M.; Ciriano, M.; Howard, J. A. K.; Murray, M.; Pugh, N. J.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 659−666. (b) Levchinsky, Y.; Rath, N. P.; Braddock-Wilking, J. *Organometallics* **1999**, *18*, 2583−2586. (c) Braddock-Wilking, J.; Levchinsky, Y.; Rath, N. P. *Organometallics* **2000**, *19*, 5500−5510.

(11) (a) Kim, Y.-J.; Lee, S.-C.; Park, J.-I.; Osakada, K.; Choi. J.-C.; Yamamoto, T. *Organometallics* **1998**, *17*, 4929−4931. (b) Kim, Y.-J.; Lee, S.-C.; Park, J.-I.; Osakada, K.; Choi. J.-C.; Yamamoto, T. *Dalton* **2000**, 417−421.

(12) (a) Butts, M. D.; Bryan, J. C.; Luo, X.-L.; Kubas, G. J. *Inorg. Chem.* **1997**, *36*, 3341. (b) Simons, R. S.; Tessier, C. A. *Organometallics* **1996**, *15*, 2604−2610. (c) Aitken, T. C.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059−4066.

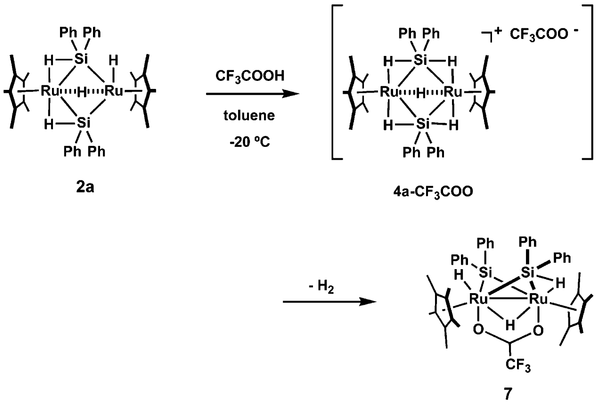
Although IR spectroscopy is a good method for observing the $\eta^2$-Si−H interaction,[1b] the $\nu$(Ru−H−Si) of **2c** was obscured by the strong absorption of the carbonyl group ($\nu$(CO) = 1756 cm$^{-1}$). The $\nu$(Ru−H) of the terminal Ru−H bond was, however, clearly seen at 2060 cm$^{-1}$, which lay in the range of the $\nu$(Ru−H) of bis($\mu$-silyl) complex **2** (2054−2092 cm$^{-1}$).[1]

The trifluoroacetoxy group was shown to be $\sigma$-bonded to the bridging silicon atom. While the Si(2)−O(1) bond length (1.760(3) Å) is slightly longer than those of other compounds that have a trifluoroacetoxy group on the silicon atom (Si(OCOCF$_3$)(OH)$_2${C(SiMe$_3$)$_3$}, 1.713 Å;[13a] Zn[C(SiMe$_3$)$_2${SiMe$_2$(OCOCF$_3$)}]$_2$, 1.726 Å[13b]), it is still shorter than the sum of the covalent radii (1.83 Å).

The trifluoroacetoxy group on Si(2) occupied the equatorial site with respect to the four-membered Ru(1)−Si(1)−Ru(2)−Si(2) ring. This was most likely due to steric repulsion between the Cp* groups and the phenyl groups. The bulkier phenyl group tends to occupy the axial position, which was far away from the two Cp* groups. The same trend was seen in the bis($\mu$-silyl) complex (Cp*Ru)$_2$($\mu$-$\eta^2$-HSi$^t$Bu$_2$)($\mu$-$\eta^2$-HSiPhH)($\mu$-H)(H) (**2d**).[1b]

While the reaction of **2a** with trifluoroacetic acid in toluene afforded the neutral bis($\mu$-silylene) complex **3b**, the cationic bis($\mu$-silane) complex **4a**-CF$_3$CO$_2$ was formed in the reaction carried out in CH$_2$Cl$_2$. In the reaction conducted in CH$_2$Cl$_2$, nucleophilic substitution of the phenyl group with a trifluoroacetoxy group at the bridging silicon atom did not occur. Although **4a**-CF$_3$CO$_2$ was not isolated, formation of **4a** was confirmed by the subsequent anion-exchange to BPh$_4^-$.[2] On the other hand, reaction of **4a**-BPh$_4$ with trifluoroacetic acid in toluene resulted in formation of the neutral bis($\mu$-silylene) complex **3b**. Benzene was detected by GC during the reaction. This implies that anion exchange from BPh$_4$ to CF$_3$COO causes Si−C(aryl) bond cleavage. Thus, it is concluded that complex **3b** was formed via initial protonation to form **4a** and that subsequent coordination of the trifluoroacetoxy anion to the ruthenium center in toluene promotes the addition of the trifluoroacetoxy group to the bridging silylene moiety.

Treatment of **2a** with trifluoroacetic acid in toluene at −20 °C resulted in the exclusive formation of a $\mu$-carboxy intermediate, (Cp*Ru)$_2$($\mu$-$\eta^2$-HSiPh$_2$)($\mu$-SiPh$_2$)($\mu$-CF$_3$CO$_2$)($\mu$-H)(H) (**7**), which has $\mu$-carboxy, $\mu$-silyl, and $\mu$-silylene groups between the ruthenium atoms (eq 6). Complex **7** was characterized by means of $^1$H, $^{13}$C, and $^{29}$Si NMR and IR spectra and analytical data. Although the relative positions of the bridging ligands could not be determined on the basis of the spectral data, we tentatively assigned complex **7** as shown in eq 6.



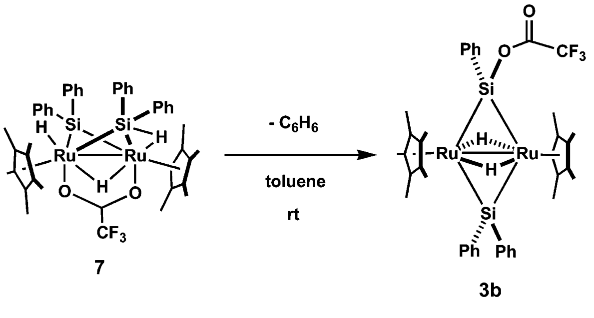
(6)

In the $^1$H NMR spectra of **7** measured at −30 °C, three signals due to the hydride ligands were observed at $\delta$ −13.35, −11.16, and −4.78, respectively. Among them, a set of satellite signals due to spin−spin coupling between $^{29}$Si and $^1$H was observed around the signal observed at $\delta$ −4.78 ($J_{\mathrm{Si-H}}$ = 60 Hz). The $J_{\mathrm{Si-H}}$ value strongly indicates the existence of a 3c-2e Ru−H−Si bond in **7**.[14] One of the two $^{29}$Si signals was observed at $\delta$ 121.7 to be a doublet ($J_{\mathrm{Si-H}}$ = 60 Hz), while the $^{29}$Si signal observed at $\delta$ 75.2 was a singlet. Thus, the former was assignable to the silicon atom comprising the 3c-2e bond, and the latter was that of the $\mu$-silylene ligand. Upon selective irradiation at each hydride signal, the intensities of the other hydride signals did not change. This implies that site-exchange of the hydride ligands was negligible within the NMR time scale at least at −20 °C.

The IR spectra of **7** showed a sharp absorption at 2058 cm$^{-1}$, which was likely assignable to the $\nu$(Ru−H) for a terminal hydride ligand. Since only one strong absorption for the $\nu$(Ru−H) was observed, the rest of the hydride ligands were considered to be bridging ones.

The integration of the phenyl groups (20H) showed that all of the phenyl groups were still bonded to the bridging silicon atoms in **7**. This indicates that Si−C(aryl) bond cleavage did not occur at this stage. Four signals of the *ipso*-carbon of the phenyl groups were observed at $\delta$ 148.8, 147.9, 147.4, and 146.6 in the $^{13}$C NMR spectra, respectively. The $^{13}$C signals coupled with the $^{19}$F nucleus were observed at $\delta$ 114.9 ($^1J_{\mathrm{C-F}}$ = 285.6 Hz) and 164.3 ($^2J_{\mathrm{C-F}}$ = 41.2 Hz) as quartets. These were assigned to the CF$_3$ group and the carbonyl carbon atoms, respectively. These results strongly indicated the coordination of the trifluoroacetoxy group in **7**.

A hypsochromic shift for the $\nu$(CO) of the trifluoroacetoxy group in **7** was observed in comparison to those for **2c** and **3b**. While $\nu$(CO) for **2c** and **3b** were 1756 and 1754 cm$^{-1}$, respectively, that for **7** was 1702 cm$^{-1}$. This indicates the bridging coordination of the trifluoroacetoxy group in **7**. This value is comparable to the $\nu$(CO) of 1656 cm$^{-1}$ for {Cp*Ru($\mu$-CF$_3$COO)($\mu$-H)}$_2$, of which the structure has been established by the X-ray diffraction study.[5]



(7)

Upon warming from −20 °C to room temperature, **7** was quantitatively converted into **3b** (eq 7). The reaction rate in toluene was almost similar to that performed in

---

(13) (a) Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B. *J. Organomet. Chem.* **1992**, *423*, 5−12. (b) Al-Juaid, S. S.; Eaborn, C.; Habtemariam, A.; Hitchcock, P. B. *J. Organomet. Chem.* **1992**, *437*, 41−55.

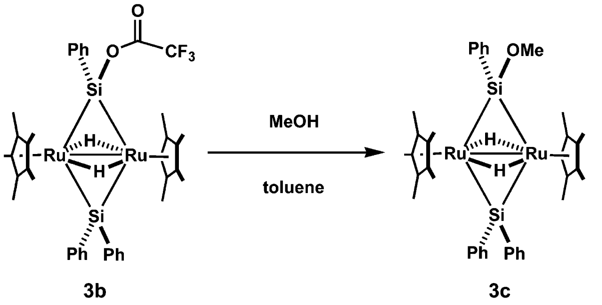
(14) Shubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151−187.

THF, which implied that **3b** was formed by way of a nonionic pathway; that is, the carboxy group was not eliminated as a carboxylate anion during the reaction. When the reaction was carried out in THF/$H_2O$ with excess amount of sodium acetate, a bis($\mu$-silylene) complex having an acetoxy group on the bridging silicon atom was not observed. Instead, complex **3b** was formed in the reaction. This result also implied the intramolecular mechanism for the substitution reaction. Instead, a bis($\mu$-silylene) complex having a hydroxyl group on the bridging silicon atom, $\{Cp^*Ru(\mu\text{-}H)\}_2\{\mu\text{-}SiPh(OH)\}(\mu\text{-}SiPh_2)$ (**3d**), was obtained in this reaction (ca. 10% by NMR). Complex **3d** was likely formed by the reaction of **3b** with $H_2O$ (vide infra).

A plausible reaction mechanism for the formation of **3b** by the reaction of **2a** with trifluoroacetic acid is shown in Scheme 1. Protonation of **2a** should take place first to yield **4a**, then the trifluoroacetoxy anion was coordinated to the metal center. The $\mu$-carboxy intermedaite **7** was formed by way of elimination of dihydrogen. Oxidative addition of the $\eta^2$-Si–H bond and subsequent nucleophilic attack of the coordinated carboxy group at the bridging silicon atom took place to form an intermediate silylene-silyl complex **I-2** probably due to the strong affinity between Si and O. Then, the Si–C(aryl) bond should be cleaved to yield **I-3**. The conversion from **I-1** to **I-3** would proceed stepwise via **I-2** probably due to the poor leaving ability of the phenyl group on the silicon. This type of Si–C(aryl) bond cleavage has been already observed in the reaction of $Cp^*Ru(\mu\text{-}H)_4RuCp^*$ (**1**) with $Ph_3SiH$ to yield bis($\mu$-diphenylsilylene) complexes $\{Cp^*Ru(\mu\text{-}SiPh_2)(\mu\text{-}H)\}_2$ (**3a**) and $\{Cp^*Ru(\mu\text{-}H)\}_2(\mu\text{-}SiPh_2)$.[1d] Although substitution reaction of the Si–C(aryl) group by way of orthometalation of the arylsilyl group has been known for the monometallic platinum silyl complex,[15] the orthometalation path requires a much higher formal oxidation state for the metal center.

The diethyl analogue of the cationic bis($\mu$-silane) complex **4b** also reacted with trifluoroacetic acid in toluene. Since the product could not be isolated due to its thermal instability, the structure could not be determined. However, the broad hydride signal observed at $\delta$ −20.99 in the crude mixture implied that a bis($\mu$-silylene) complex was also formed, and $\nu$(CO), which appeared at 1749 $cm^{-1}$, also implied that the ethyl group on the bridging silicon was substituted with the trifluoroacetoxy group.

**Nucleophilic Displacement at the Bridging Silicon Atom of 3b.** The trifluoroacetoxy group of **3b** was readily converted to other functional groups by nucleophilic displacement. Treatment of **3b** with MeOH resulted in the formation of the bis($\mu$-silylene) complex $\{Cp^*Ru(\mu\text{-}H)\}_2\{\mu\text{-}SiPh(OMe)\}(\mu\text{-}SiPh_2)$ (**3c**), containing a methoxy group on the bridging silicon (eq 8). Complex

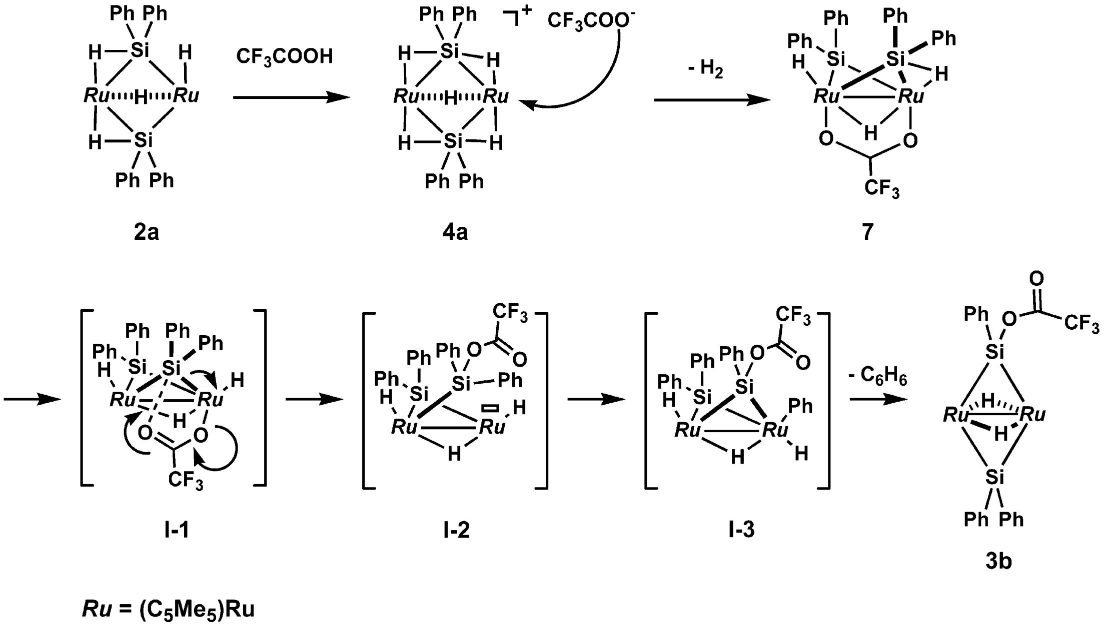


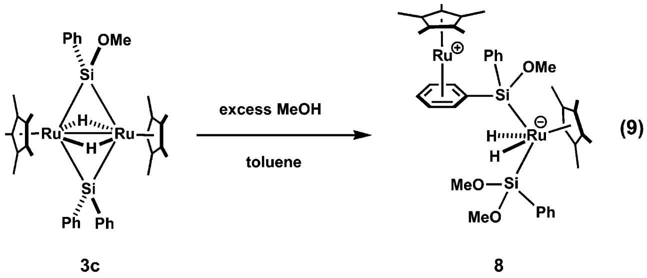
(8)

**3c** was characterized by its $^1H$, $^{13}C$, and $^{29}Si$ NMR and IR spectra. Although the structure of **3c** was not determined by X-ray diffraction because of difficulty in obtaining a single crystal, complex **3c** was concluded to be a *trans*-bis($\mu$-silylene) structure like **3a** and **3b** on the basis of its spectral data and fluxional behavior.

Complex **3c** underwent further addition of methanol, and a prolonged reaction afforded the zwitterionic $\eta^6$-arene complex $Cp^*Ru^+(\eta^6\text{-}C_6H_5[SiPh(OMe)\{Cp^*Ru^-(H)_2\text{-}Si(OMe)_2Ph\}])$ (**8**) (eq 9). During the formation of **8**, two Ru–Si bonds were cleaved, and one of the phenyl groups on the silicon atom coordinated to one of the Ru centers in an $\eta^6$-fashion. Thus, complex **8** may be regarded as an intermediate in the formation of the $\eta^6$-benzene complex $[Cp^*Ru(\eta^6\text{-}C_6H_6)]^+$ (**5**) by treatment of **4a** with

**Scheme 1**





**3c** **8** (9)

methanol, which was apparently formed as a result of Ru−Si and Si−C(aryl) bond cleavage. Complex **8** was isolated as a colorless crystalline solid, and the structure was determined by means of X-ray diffraction studies.

Nucleophilic attack of methoxides at the bridging silicon atoms leads to cleavage of the Ru−Si bonds and the Ru−Ru bond, and the Cp*Ru fragment was bound to one of the phenyl groups on the silicon atom in an $\eta^6$-fashion.

The structure of complex **8** is illustrated in Figure 2, and the relevant bond distances and angles are listed in Table 2. The two ruthenium atoms are apart from each other by 5.86 Å, and there is no bonding interaction between them. Since complex **8** is diamagnetic, the formal oxidation states of Ru(1) and Ru(2) should be +4 and +2, respectively. Coordination geometry around Ru(2) is very similar to that of $[\mathrm{Cp^*Ru}(\eta^6\text{-arene})]^+$,[16] and the angle among the centroids of the Cp*, Ru(2), and the centorid of the phenyl group is almost linear (179.0°). This shows that Ru(2) is charged monocationic and the Ru(1) center is, therefore, monoanionic.

The coordination geometry around Ru(1) is that of a four-legged piano stool. Both silicon atoms, Si(1) and Si(2), and two hydrogen atoms, H(1) and H(2), are mutually *trans* with respect to the Ru(1) center. The partial structure of **8** around Ru(1) is isoelectronic with *trans*-bis(silyl) complexes, $\mathrm{Cp^*M(SiR_3)_2(H)_2}$ (M = Co,[17] Rh,[18] Ir[19]) and $(\eta^6\text{-}\mathrm{C_6R_6})\mathrm{M(SiR_3)_2(H)_2}$ (M = Fe,[20] Ru[21]), on account of the formal minus charge on Ru(1). A characteristic feature of the structure of **8** is the relatively short Ru−Si distances, 2.3107(17) Å for Ru(1)−Si(1) and 2.3116(17) Å for Ru(1)−Si(2). Although the Ru−Si bond lengths lie within the reported range for the Ru−Si $\sigma$-bonds (2.28−2.50 Å),[22] they are considerably shorter than those of $(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{Ru(SiMe_3)_2(H)_2}$ (2.396(1) and 2.391(1) Å).[21] The shortening of the Ru−Si bonds in **8** is most likely due to enhanced d$\pi$−d$\pi$ interaction between Ru(1) and the silicon atoms as a result of an anionic charge on Ru(1).

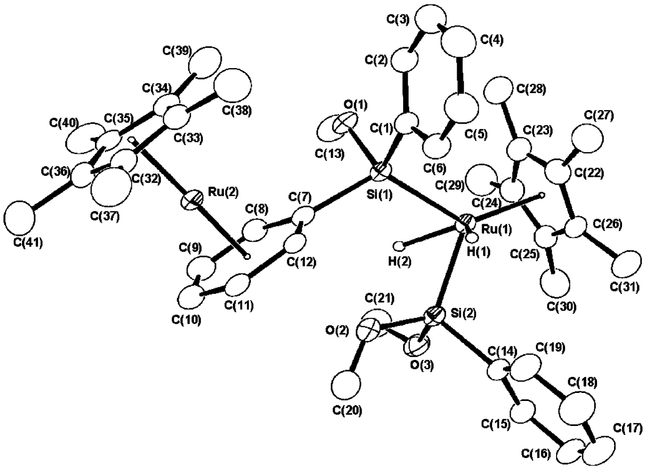
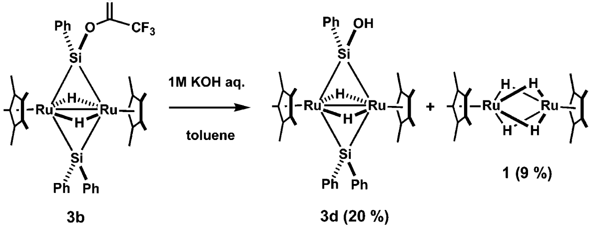


**Figure 2.** Molecular structure of $\mathrm{Cp^*Ru^+}(\eta^6\text{-}\mathrm{C_6H_5}[\mathrm{SiPh(OMe)}\{\mathrm{Cp^*Ru^-(H)_2Si(OMe)_2Ph}\}])$ (**8**) with thermal ellipsoids at the 30% probability level. The solvent molecules were omitted for clarity.

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

| | | | |
|---|---|---|---|
| Ru(1)−Si(1) | 2.3107(17) | Ru(1)−Si(2) | 2.3116(17) |
| Ru(2)- C(7) | 2.293(6) | Ru(2)- C(8) | 2.225(6) |
| Ru(2)- C(9) | 2.197(7) | Ru(2)- C(10) | 2.216(6) |
| Ru(2)- C(11) | 2.208(6) | Ru(2)- C(12) | 2.233(6) |
| Si(1)−C(1) | 1.886(6) | Si(1)−C(7) | 1.924(6) |
| Si(1)−O(1) | 1.676(4) | Si(2)−C(14) | 1.896(7) |
| Si(2)−O(2) | 1.658(5) | Si(2)−O(3) | 1.691(5) |
| Si(1)−Ru(1)−Si(2) | 106.07(6) | Ru(1)−Si(1)−O(1) | 118.21(17) |
| Ru(1)−Si(1)−C(1) | 114.82(19) | Ru(1)−Si(1)−C(7) | 114.84(17) |
| O(1)−Si(1)−C(1) | 99.2(3) | O(1)−Si(1)−C(7) | 101.8(2) |
| C(1)−Si(1)−C(7) | 105.9(3) | Ru(1)−Si(2)−O(2) | 114.16(16) |
| Ru(1)−Si(2)−O(3) | 117.84(18) | Ru(1)−Si(2)−C(14) | 117.2(2) |
| O(2)−Si(2)−O(3) | 104.9(3) | O(2)−Si(2)−C(14) | 102.6(3) |
| O(3)−Si(2)−C(14) | 97.8(3) | | |

A $\mu$-hydroxysilylene complex, $\{\mathrm{Cp^*Ru}(\mu\text{-H})\}_2\{\mu\text{-SiPh(OH)}\}(\mu\text{-SiPh_2})$ (**3d**), was obtained in 20% yield by the treatment of **3b** with aqueous KOH at ambient temperature for 12 h (eq 10). The reaction is much slower than that of **3b** with MeOH shown in eq 8. While the reaction of **3b** with MeOH was homogeneous and terminated within 1 h, that of **3b** with aqueous KOH was biphasic and only 36% of **3b** was consumed after 12 h. The yield of **3d** was estimated at 20% on the basis of the $^1$H NMR spectra, and a small amount of unidentified byproducts was formed during the reaction together with the dinuclear tetrahydride complex **1** (9% yield). Complex **3d** was alternatively synthesized by the reaction of **4a**-OTf, which was prepared in situ by reaction of **2a** with trifluoromethanesulfonic acid, with adventitious water absorbed on alumina in 56% yield (eq 11), and characterized on the basis of the $^1$H, $^{13}$C, and $^{29}$Si NMR and IR spectra. Although a single crystal of **3d** suitable for the diffraction studies was not



**3b** **3d** (20 %) **1** (9 %) (10)

---

[15] Chang, L. S.; Johnson, M. P.; Fink, M. J. *Organometallics* **1991**, *10*, 1219−1221.

[16] (a) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698−1719. (b) Ward, M. D.; Fagan, P. J.; Calabrese, J. C.; Johnson, D. C. *J. Am. Chem. Soc.* **1989**, *111*, 1719−1732.

[17] Brookhart, M.; Grant, B. E.; Lenges, C. P.; Prosenc, M. H.; White, P. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1676−1679.

[18] Fernandez, M.-J.; Bailey, P. M.; Bentz, P. O.; Ricci, J. S.; Koetzle, T. F.; Maitlis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 5458−5463.

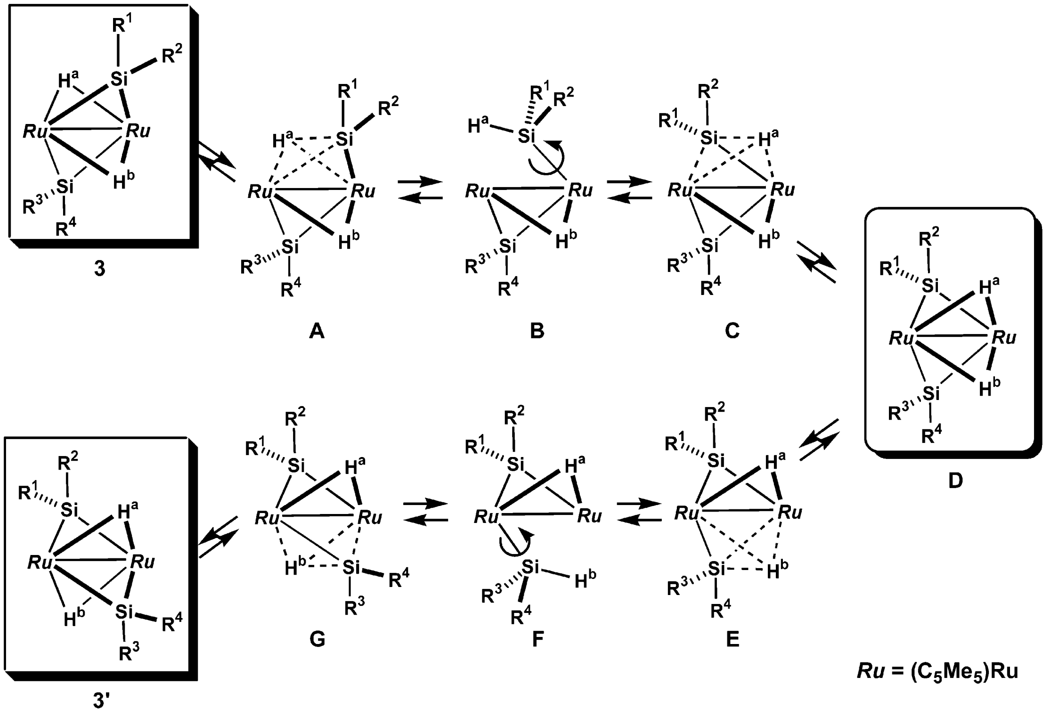
[19] Ricci, J. S.; Koetzle, T. F.; Fernandez, M.-F.; Maitlis, P. M.; Green, J. C. *J. Organomet. Chem.* **1986**, *299*, 383−389.

[20] (a) Klabunde, K. J.; Yao, Z.; Hupton, A. C. *Inorg. Chim. Acta* **1997**, *259*, 119−124. (b) Yao, Z.; Klabunde, K. J.; Asirvatham, A. S. *Inorg. Chem.* **1995**, *34*, 5289−5294. (c) Yao, Z.; Klabunde, K. J. *Organometallics* **1995**, *14*, 5013−5014. (d) Asirvatham, V. S.; Yao, Z.; Klabunde, K. J. *J. Am. Chem. Soc.* **1994**, *116*, 5493−5494.

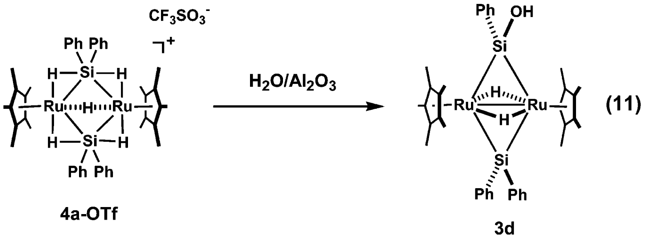
[21] Djurovich, P. I.; Carroll, P. J.; Berry, D. H. *Organometallics* **1994**, *13*, 2551−2533.

[22] Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175−292.

**Scheme 2**



obtained, complex **3d** was concluded to have the same structure as **3a** and **3b** on the basis of the spectral data.



(11)

Substitution of a phenyl group on the bridging silyl group with a hydroxy group would be accelerated by the cationic charge on the ruthenium center. A similar reaction has been reported for a platinum silyl complex.[15]

Complex **3d** is a dimetallosilanol, in which the Si−OH group is directly bound to the metal atom. Reactivities of metallosilanols, M−Si−OH, have been well documented by Malisch et al.[6f,23] It has been shown that the metallosilanols are less acidic than organosilanols due to the strong electron-releasing nature of the metal fragment, and as a result, the tendency toward self-condensation is noticeably diminished. Complex **3d** is stable and did not undergo self-condensation similar to $\{CpFe(CO)_2\}_2(\mu\text{-SiROH})$ (R = Me, p-Tol, H, Cl, and OH). The interatomic distance between the two ruthenium atoms in $\{Cp^*Ru(\mu\text{-H})(\mu\text{-SiPh}_2)\}_2$ (**3a**) is 2.665 Å.[1a,d] Complex **3d** would adopt a similar structure to **3a** on the basis of spectral data; therefore, a direct metal−metal bond seems to exist in **3d**. In contrast, bis(ferrio)silanol $\{CpFe(CO)_2\}_2\{\mu\text{-Si(H)OH}\}$ has no bonding interaction between the two iron atoms, and the Fe−Fe separation is very large (4.12 Å). Thus, to the best of our knowledge, complex **3d** is the first example of a dimetallosilanol containing a direct metal−metal bonding interaction.

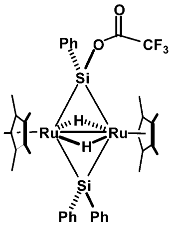
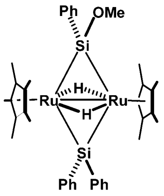
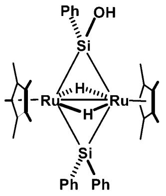
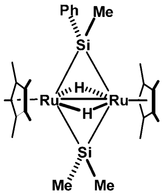
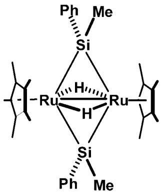
In the $^1$H NMR spectra of **3d** measured in $C_6D_6$, the hydroxy proton was observed at $\delta$ 1.30 as a broad peak. The resonances of the hydride ligands were observed at $\delta$ −20.50 and −20.04 as doublets with $J_{H-H}$ = 5.8 Hz at −50 °C in THF-$d_8$. The $^1$H NMR spectra of **3d** showed temperature dependence quite similar to those of **3b** and **3c**. In the $^1$H NMR spectra, the two hydride ligands in **3b**, **3c**, and **3d** were observed to be inequivalent at low temperature, but these signals coalesced into one signal at elevated temperature due to rapid exchange of the coordination site.

**Site-Exchange of the Hydride Ligands of Bis(*μ*-silylene) Complexes.** The hydride ligands of the bis(*μ*-silylene) complex **3** mutually exchange coordination sites via a *cis*-bis(*μ*-silylene) intermediate **D**, as shown in Scheme 2. We previously reported the hydride site-exchange reaction in bis(*μ*-silylene) complexes $\{Cp^*Ru(\mu\text{-H})\}_2(\mu\text{-SiMe}_2)(\mu\text{-SiPhMe})$ (**3e**) and $\{Cp^*Ru(\mu\text{-H})(\mu\text{-SiPhMe})\}_2$ (**3f-*syn***), and the activation parameters were estimated as $\Delta H^\ddagger = 16.4 \pm 0.7$ kcal mol$^{-1}$ and $\Delta S^\ddagger = 15.5 \pm 2.7$ cal mol$^{-1}$ K$^{-1}$ for **3e** and $\Delta H^\ddagger = 16.7 \pm 0.4$ kcal mol$^{-1}$ and $\Delta S^\ddagger = 12.5 \pm 1.5$ cal mol$^{-1}$ K$^{-1}$ for **3f-*syn***, respectively (Table 3).[1d] While **3e** and **3f-*syn*** contain a *μ*-SiPhMe bridge, the substituents on the second silylene bridge are different; complex **3e** possesses a *μ*-SiMe$_2$ bridge in place of the additional *μ*-SiPhMe bridge in **3f-*syn***. Irrespective of the different combination of substituents on the bridging silicon atoms in **3e** and **3f-*syn***, activation parameters for the hydride site-exchange reaction are the same within experimental error. These facts imply that the electronic nature of substituents on the bridging silicon does not influence the activation parameters of the hydride site-exchange reaction.

---

[23] (a) Malisch, W.; Jehle, H.; Möller, S.; Saha-Möller, C.; Adam, W. *Eur. J. Inorg. Chem.* **1998**, 1585−1587. (b) Malisch, W.; Hofmann, M.; Kaupp, G.; Käb, H.; Reising, J. *Eur. J. Inorg. Chem.* **2000**, 3235−3241.

**Table 3. Activation Parameters of the Hydride Site-Exchange Process of Bis($\mu$-silylene) Complexes**

| | <br>**3b** | <br>**3c** | <br>**3d** | <br>**3e** [1d] | <br>**3f-*syn*** [1d] |
|---|---|---|---|---|---|
| **$\Delta H^‡$ (kcal mol$^{-1}$)** | 12.8 ± 0.4 | 13.6 ± 0.3 | 14.9 ± 0.2 | 16.4 ± 0.7 | 16.7 ± 0.4 |
| **$\Delta S^‡$ (cal mol$^{-1}$ K$^{-1}$)** | 1.9 ± 1.5 | 5.1 ± 1.5 | 9.9 ± 0.9 | 15.5 ± 2.7 | 12.5 ± 1.5 |
| **$\Delta G_{300K}^‡$ (kcal mol$^{-1}$)** | 12.2 | 12.1 | 11.9 | 11.8 | 13.0 |
| **$\delta$ $^{29}$Si [a] *Si*PhX (SiR$_2$)** | *137.5*<br>(109.2) | *133.6*<br>(98.2) | *128.0*<br>(97.1) | *107.9*<br>(112.3) | *108.2*<br>(108.2) |

[a] $^{29}$Si{$^1$H} NMR spectra for **3b**, **3c**, and **3d** were recorded at ambient temperature in benzene-$d_6$.

We examined the influence of the substituents on the fluxional process using the new bis($\mu$-silylene) complexes **3b**−**d** containing an O-functionalized group on the bridging silicon atom as the probes. At −65 °C, hydride signals of **3b** appeared at $\delta$ −18.50 and −20.17 as two doublet peaks with $J_{\mathrm{H-H}}$ = 5.6 Hz. They coalesced into one peak at 10 °C. Activation parameters of this process were estimated at $\Delta H^‡ = 12.8 \pm 0.4$ kcal mol$^{-1}$ and $\Delta S^‡ = 1.9 \pm 1.5$ cal mol$^{-1}$ K$^{-1}$ on the basis of the line shape analysis. Introduction of the trifluoroacetoxy group resulted in a decrease of $\Delta H^‡$ and $\Delta S^‡$ by ca. 4 kcal/mol and ca. 10 eu, respectively, in comparison to those of **3e** and **3f-*syn*** (Table 3).

The difference in the activation parameters between **3b** and **3e** most likely stems from the difference in the electronic nature of the substituents on the silicon atom. The electron-withdrawing trifluoroacetoxy group reduces the electron density at the silicon atom. The effect of the electronic nature of the substituents was also reflected in the $^{29}$Si NMR spectra. While the $^{29}$Si signal of **3b** was observed at $\delta$ 137.5, those of the phenylmethylsilylene group of **3e** and **3f-*syn*** were observed at $\delta$ 107.9 and 108.2, respectively. The downfield shift of the $^{29}$Si signal of **3b** is probably attributable to the reduction of electron density at the silicon atom due to introduction of the electron-withdrawing substituent. Thus, on the basis of the $^{29}$Si NMR data, the electron-withdrawing nature of the substituent on the bridging silicon atom would lie in the order $CF_3CO_2 > OMe > OH > Me$.

Lichtenberger et al. elucidated that the electronic nature of the substituents on a silicon atom significantly influenced the energy level of the $\sigma^*$(Si−H) as studied by photoelectron spectroscopy.[8] An electron-withdrawing group on the silicon atom has been shown to lower the energy level of the $\sigma^*$(Si−H). This would facilitate the Si−H bond cleavage due to enhanced back-donation from the metal center. In contrast, the electron-donating methyl group on the bridging silicon atom reduces the back-donation, and as a result, the $\eta^2$-Si−H coordination would be favored.

As shown in Table 3, a linear correlation between the electronic nature of the substituents on the bridging silicon atom and activation parameters of the hydride site-exchange process was clearly seen; the electron-withdrawing substituent OR (R = $CF_3CO_2$, OMe, OH) on the bridging silicon atom decreases both $\Delta H^‡$ and $\Delta S^‡$ in comparison with the methyl group in **3e** and **3f-*syn***. Thus, the activation parameters of the fluxional process would have a close relationship with the strength of the Si−H bond in the transition state for the site-exchange. These results indicate that the rate-determining step of the site-exchange process involves formation and cleavage of an Si−H bond, and the resonance hybrid of the transition state is likely influenced by the electronic nature of the substituents. The reason the parameters of **3e** and **3f-*syn*** were the same was thus attributed to the $\mu$-SiPhMe bridge common in the structures.

The activation parameters were highly affected by the electronic nature of the substituents, which strongly indicates the participation of the transient $\mu$-silyl complex during the site-exchange process of the hydride ligands of the bis($\mu$-silylene) complex **3**. This also suggests that the rate-determining step of the site-exchange process most likely includes the formation and cleavage of the $\eta^2$-coordinated Si−H bond (**A**, **C**, **E**, or **F** in Scheme 2). Similar transformation of the $\mu$-silylene ligand to a transient $\mu$-silyl group also has been proposed for the dirhodium complex $Rh_2(\mu\text{-SiRH})H_2(CO)_2(dppm)_2$ by Eisenberg and co-workers, in which rapid exchange between the Si−H and Rh−H took place.[24]

## Conclusion

Treatment of the bis($\mu$-diphenylsilyl) complex **2a** with trifluoroacetic acid in toluene resulted in the exclusive formation of the mixed-bridging bis($\mu$-silylene) complex **3b**, which contained a trifluoroacetoxy group on the bridging silicon atom. This is in sharp contrast to protonation carried out in $CH_2Cl_2$, which afforded cationic bis($\mu$-silane) complexes. These results mean that protonation of the bis($\mu$-silylene) complex was highly affected by the solvent and nucleophilicity of the counteranion. Nucleophilic addition of the trifluoroacetoxy group to the ruthenium centers was confirmed by the observation of the intermediate $\mu$-silyl,$\mu$-silylene complex **7**, containing a $\mu$-carboxy group. The carboxy group would move to the bridging silicon atom, forming an intermediary $\mu$-silyl group. Subsequent Si−C(aryl) bond cleavage then resulted in formation of **3b**.

Complex **3b** is a good precursor for functionalized $\mu$-silylene complexes. Treatment of **3b** with MeOH and $H_2O$ afforded **3c** and **3d**, which contained a methoxy and a hydroxy group at the bridging silicon atom, respectively. There have been quite limited examples of nucleophilic displacement reaction performed on the bridging silicon atom, and introduction of the hydroxy group on the bridging silicon atom by way of protonation was a novel synthetic method for the dimetallosilanols. Since the stereochemistry at the bridging silicon of the bis($\mu$-silylene) complex **3** was not maintained due to 1,2-shift of the intermediary $\mu$-silyl group,[1d] at present the substitution reaction cannot be precisely clarified as to whether it proceeds by an $S_N1$ or $S_N2$ mechanism.

Isolation of the various bis($\mu$-silylene) complexes **3a**−**f**, which contain various substituents on the bridging silicon atom, allowed us to understand the fluxional process of **3** in detail. VT-NMR studies revealed that the activation parameters were significantly influenced by the electronegativity of the substituents on the bridging silicon. An electron-withdrawing substituent on the bridging silicon atom decreases both $\Delta H^\ddagger$ and $\Delta S^\ddagger$, and an electron-donating one increases them. This phenomenon can be explained by the mechanism in which the hydride site-exchange proceeds by the formation of an intermediate silyl complex as a result of reductive coupling between the $\mu$-silylene ligand and hydride. Rotation of the silyl group and oxidative addition of the Si−H bond should result in formation of the *cis*-bis($\mu$-silylene) intermediate. Subsequent formation of the silyl group by reductive coupling between the other $\mu$-silylene and hydride ligands would complete the site-exchange of the hydride ligands.

Formation of the intermediate Si−H bond is relevant to the formation of a vacant site on the dinuclear system. If there were substrates that can react with a bis($\mu$-silylene) complex, reactivities of the bis($\mu$-silylene) complexes should show linear correlation with the activation parameters obtained by the NMR studies. We are continuing research on the reactivity of the bis($\mu$-silylene) complexes. In particular, we will focus on the influence of the electronic nature of the substituents on the bridging silicon atom on the reactivity of the $\mu$-silylene ligand.

## Experimental Section

**General Procedures.** All experiments were carried out under an argon atmosphere. All compounds were handled using Schlenk techniques. Reagent grade toluene, $Et_2O$, and THF were dried over sodium-benzophenone ketyl and stored under an argon atmosphere. Pentane and dichloromethane were 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. Trifluoroacetic acid 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. $^{29}Si$ NMR spectra were recorded on JEOL EX-270 and Varian INOVA-400 instruments with tetramethylsilane as an external standard. Elemental analyses were performed by the Analytical Facility at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology. The dinuclear ruthenium tetrahydride complex $Cp^*Ru(\mu\text{-}H)_4RuCp^*$ (**1**),[25] the bis($\mu$-diphenylsilyl) complex $\{Cp^*Ru(\mu\text{-}\eta^2\text{-}HSiPh_2)\}_2(\mu\text{-}H)(H)$ (**2a**),[1a] the bis($\mu$-diphenylsilylene) complex $\{Cp^*Ru(\mu\text{-}SiPh_2)(\mu\text{-}H)\}_2$ (**3a**),[1a] and the cationic bis($\mu$-silane) complex $[\{Cp^*Ru(\mu\text{-}\eta^2{:}\eta^2\text{-}H_2SiR_2)\}_2(\mu\text{-}H)][X^-]$ (**4a**, R = Ph; **4b**, R = Et, X = $CF_3SO_3$, $BPh_4$)[2] were prepared according to previously published methods. Formation of the cationic $\eta^6$-benzene complex $[Cp^*Ru(\eta^6\text{-}C_6H_6)]^+$ (**5**) shown in eq 3 was confirmed on the basis of the $^1H$ NMR data by comparing with the authentic complex prepared according to previously published methods.[5,25a] Formation of the cationic triruthenium hexahydride complex $[Cp^*Ru(\mu\text{-}H)_2]_3{}^+$ (**6**) shown in eq 3 was confirmed on the basis of the $^1H$ NMR data by comparing with the authentic complex prepared according to the reported method.[5]

**X-ray Structure Determination.** X-ray-quality crystals of **2c** and **8** were obtained directly from the preparations described below and mounted on glass fibers. Diffraction experiments were performed on a Rigaku RAXIS-RAPID imaging plate at −20 °C for **2c** and on a Rigaku AFC-5R four-circle diffractometer at 23 °C for **8** with graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71069 Å), respectively. The structures of **2c** and **8** were solved by a direct method and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculation on $F^2$ using the SHELXL-97 program package.[26] The positions of hydrogen atoms bonded to the ruthenium atoms of **2c** and **8** were located by the sequential difference Fourier synthesis. Neutral atom scattering factors were obtained from the standard sources.[27] Crystal data and results of the analyses are listed in Table 4.

**Variable-Temperature NMR Spectra and Dynamic NMR Simulations.** Variable-temperature NMR studies were performed in flame-sealed NMR tubes in toluene-$d_8$ for **3b**−**d** using a Varian INOVA-400 Fourier transform spectrometer. NMR simulations for the hydride ligands of **3b**−**d** were performed using gNMR v4.1.0. (©1995−1999 Ivory Soft). The $^1H-{}^1H$ coupling constants between hydride ligands were

---

[24] (a) Wang, W.-D.; Eisenberg, R. *J. Am. Chem. Soc.* **1990**, *112*, 1833−1841. (b) Wang, W.-D.; Eisenberg, R. *Organometallics* **1992**, *11*, 908−912. (c) Wang, W.-D.; Hommeltoft, S. I.; Eisenberg, R. *Organometallics* **1988**, *7*, 2417−2419.

[25] (a) Suzuki, H.; Omori, H.; Lee, D.-H.; Yoshida, Y.; Moro-oka, Y. *Organometallics* **1988**, *7*, 2243−2245. (b) Suzuki, H.; Omori, H.; Lee, D.-H.; Yoshida, Y.; Fukushima, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1984**, *13*, 1129−1146.

[26] (a) Sheldrick, G. M. *SHELXS-97*, Program for Crystal Structure Solution; University of Gottingen: Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Solution; University of Gottingen, Germany, 1997.

[27] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1975; Vol. 4.

**Table 4. Crystallographic Data for 2c and 8**

| | **2c** | **8** |
|---|---|---|
| | (a) Crystal Parameters | |
| formula | $C_{40}H_{49}F_3O_2Ru_2Si_2$ | $C_{56}H_{71}O_3Ru_2Si_2$ |
| fw | 877.11 | 1050.45 |
| cryst syst | monoclinic | triclinic |
| space group | $P2_1/a$ | $P\bar{1}$ |
| $a$, Å | 14.922(3) | 13.3038(19) |
| $b$, Å | 15.2334(18) | 17.652(3) |
| $c$, Å | 17.2535(3) | 12.608(3) |
| α, deg | | 104.194(17) |
| $\beta$, deg | 95.452(8) | 110.127(13) |
| $\gamma$, deg | | 78.481(14) |
| $V$, Å$^3$ | 3904.1(12) | 2673.5(9) |
| $Z$ | 4 | 2 |
| $D_{calcd}$, g cm$^{-1}$ | 1.492 | 1.305 |
| temp, °C | −20 | 23 |
| $\mu$(Mo Kα), cm$^{-1}$ | 8.82 | 6.50 |
| cryst dimens, mm | 0.50 × 0.30 × 0.20 | 0.20 × 0.10 × 0.10 |
| | (b) Data Collection | |
| diffractometer | Rigaku AFC-5R | Rigaku AFC-5R |
| radiation | Mo Kα ($\lambda$ = 0.71069 Å) | Mo Kα ($\lambda$ = 0.71069 Å) |
| monochromator | graphite | graphite |
| scan type | $\omega/2\theta$ | $\omega/2\theta$ |
| $2\theta_{max}$, deg | 60.0 | 50.0 |
| absorp corr type | empirical | $\varphi$ scan |
| no. of reflns measd | 11 077 | 9389 |
| no. of reflns obsd | 7197 ($I > 2\sigma$) | 6611 ($I > 2\sigma$) |
| | (c) Refinement | |
| R1 [$I > 2\sigma$] | 0.0493 | 0.0651 |
| R1 (all data) | 0.0850 | 0.1017 |
| wR2 [$I > 2\sigma$] | 0.1034 | 0.1586 |
| wR2 (all data) | 0.1145 | 0.1774 |
| no. of params | 552 | 622 |
| GOF on $F^2$ | 0.942 | 1.032 |

estimated at $J_{H-H}$ = 5.60 Hz for **3b**, 5.67 Hz for **3c**, and 5.25 Hz for **3d**, respectively. The coupling constants between hydrides and the bridging silicon atoms were estimated at $^2J_{Si-H}$ = 4.00−9.00 Hz from the line shapes of satellite signals around the resonance of the hydride ligands. In the case of **3b**, small spin−spin coupling with $^{19}F$ of the trifluoroacetoxy group was observed for the hydride signals ($J_{H-F}$ = 1.10, 0.95 Hz). 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 $k$ that accurately modeled the experimental spectra at each temperature are also given in the Supporting Information. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined from the plot of ln($k/T$) versus 1/$T$. Estimated standard deviations ($\sigma$) in the slope and $y$-intercept of the Eyring plot determined the error in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively. The standard deviation in $\Delta G^{\ddagger}$ 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-SiPh(OCOCF$_3$)}(μ-SiPh$_2$) (3b).** A 100 mL flask was charged with toluene (35 mL) and {Cp*Ru(μ-η$^2$-HSiPh$_2$)}$_2$(μ-H)(H) (**2a**) (0.999 g, 1.19 mmol). After the reaction flask was cooled at −20 °C, trifluoroacetic acid (0.10 mL, 1.30 mmol) was added with vigorous stirring. The solution was allowed to react for 2 h at −20 °C, and the color of the solution turned from orange to dark red. The flask was then warmed to room temperature with bubbling argon gas into the solution to remove dihydrogen, and the solution was stirred for 2 h at 23 °C. The solvent was then removed under reduced pressure. The red residual solid was rinsed three times with 5 mL of pentane. The solid was dried under reduced pressure, and 0.827 g of **3b** was obtained as a red solid (80% yield). $^1H$ NMR (400 MHz, 21 °C, toluene-$d_8$): $\delta$ −19.43 (br, 2H, Ru$H$), 1.40 (s, 30H, Cp*), 7.9−7.0 (m, 15H, Ph). $^1H$ NMR (400 MHz, −65 °C, toluene-$d_8$): $\delta$ −20.17 (d, $J_{H-H}$ = 5.60 Hz, Ru$H$), −18.50 (d, $J_{H-H}$ = 5.60 Hz, Ru$H$), 1.39 (s, 30H, Cp*), 8.5−7.0 (m, 15H, Ph). $^{13}C$ NMR (125 MHz, 23 °C, THF-$d_8$): $\delta$ 10.9 (q, $J_{C-H}$ = 126.9 Hz, $C_5Me_5$), 92.1 (s, $C_5Me_5$), 116.2 (q, $J_{C-F}$ = 289.2 Hz, CF$_3$), 135.9 (d, $J_{C-H}$ = 159.2 Hz, Ph), 137.8 (d, $J_{C-H}$ = 156.7 Hz, Ph), 138.3 (d, $J_{C-H}$ = 158.4 Hz, Ph), 143.1 (s, Ph-ipso), 145.0 (s, Ph-ipso), 145.1 (s, Ph-ipso), 155.7 (q, $^2J_{C-F}$ = 40.4 Hz, $C$OCF$_3$). Whereas 12 signals were expected to be observed for the three phenyl groups, only six signals can be identified because of the overlap of the signals. IR (KBr, cm$^{-1}$): 3068, 2984, 2902, 1754 ($\nu$(CO)), 1678, 1483, 1429, 1377, 1212, 1164 ($\nu$(CF)), 1096, 1033, 733, 698, 675. Anal. Calcd for $C_{40}H_{47}O_2F_3Ru_2Si_2$: C, 54.90; H, 5.42. Found: C, 54.96; H, 5.14.

**Preparation of (Cp*Ru)$_2$(μ-η$^2$-HSiPh$_2$){μ-η$^2$-HSiPh(OCOCF$_3$)}(μ-H)(H) (2c).** A 50 mL flask was charged with toluene (15 mL) and {Cp*Ru(μ-H)}$_2${μ-SiPh(OCOCF$_3$)}(μ-SiPh$_2$) (**3b**) (0.175 g, 0.20 mmol) under 1 atm of H$_2$. The solution was stirred for 2 h at 23 °C, and the color of the solution changed from red to pale orange. After removal of the solvent in vacuo, a residual solid was extracted three times with 5 mL of pentane. The combined extracts were then dried under reduced pressure. Complex **2c** was obtained as an orange crystalline solid (0.153 g, 87% yield). $^1H$ NMR (500 MHz, −90 °C, THF-$d_8$): $\delta$ −14.32 (s, 1H, Ru$H$Ru or Ru$H$), −12.86 (s, 1H, Ru$H$Si), −12.46 (s, 1H, Ru$H$Si), −11.40 (s, 1H, Ru$H$Ru or Ru$H$), 1.84 (s, 15H, Cp*), 2.07 (s, 15H, Cp*), 6.7−7.4 (m, 15H, Si$Ph$). $^1H$ NMR (500 MHz, 50 °C, THF-$d_8$): $\delta$ −12.74 (br, 4H, Ru$H$), 1.96 (s, 30H, Cp*), 2.07 (s, 15H, Cp*), 7.0−7.4 (m, 15H, Si$Ph$). $^{13}C\{^1H\}$ NMR (100 MHz, 23 °C, benzene-$d_6$): $\delta$ 11.8 ($C_5Me_5$), 95.8 ($C_5Me_5$), 115.9 (q, $J_{C-F}$ = 288.0 Hz, CF$_3$), 127.0 (Ph), 127.3 (Ph), 128.8 (Ph), 133.4 (Ph), 134.7 (Ph), 137.0 (Ph), 142.1 (Ph-ipso), 144.7 (Ph-ipso), 146.1 (Ph-ipso), 155.8 (q, $^2J_{C-F}$ = 40.2 Hz, $C$OCF$_3$). Whereas 12 signals were expected to be observed for the three phenyl groups, only 9 signals can be identified because of the overlap of the signals with those of the solvent. $^{29}Si\{^1H\}$ NMR (54 MHz, 23 °C, benzene-$d_6$): $\delta$ 80.5 (μ-$Si$Ph$_2$), 129.4 (μ-$Si$PhOCOCF$_3$). IR (KBr, cm$^{-1}$): 3064, 2966, 2906, 2060 ($\nu$(RuH)), 1756 ($\nu$(CO)), 1479, 1429, 1381, 1212, 1164 ($\nu$(CF)), 1102, 1027, 737, 698. Anal. Calcd for $C_{40}H_{49}O_2F_3Ru_2Si_2$: C, 54.76; H, 5.64. Found: C, 54.32; H, 5.71.

**Treatment of {Cp*Ru(μ-η$^2$-HSiPh$_2$)}$_2$(μ-H)(H) (2a) with Trifluoroacetic Acid in Dichloromethane.** A 50 mL flask was charged with dichloromethane (10 mL) and {Cp*Ru(μ-η$^2$-HSiPh$_2$)}$_2$(μ-H)(H) (**2a**) (0.050 g, 0.059 mmol). After the reaction flask was cooled at −78 °C with a dry ice/methanol bath, trifluoroacetic acid (5 μL, 0.065 mmol) was added with vigorous stirring. The solution was then slowly warmed to room temperature. After stirring for 5 min at room temperature, a large excess amount of NaBPh$_4$ was added. The product was extracted three times with 10 mL of CH$_2$Cl$_2$, and the combined extract was passed through Celite on a glass filter. After the solvent was removed in vacuo, the residual solid was rinsed five times with 5 mL of pentane. Removal of pentane in vacuo afforded 54 mg of **4a**-BPh$_4$ as a yellow solid (yield 79%). Identification to **4a**-BPh$_4$ was carried out by comparing its spectral data with that prepared according to the reported method.[2]

**Preparation of (Cp*Ru)$_2$(μ-η$^2$-HSiPh$_2$)(μ-SiPh$_2$)(μ-CF$_3$CO$_2$)(μ-H)(H) (7).** A 50 mL flask was charged with toluene (5 mL) and {Cp*Ru(μ-η$^2$-HSiPh$_2$)}$_2$(μ-H)(H) (**2a**) (0.118 g, 0.14 mmol). After the reaction flask was cooled to −20 °C, trifluoroacetic acid (11 μL, 0.15 mmol) was added with vigorous stirring. The solution was allowed to react for 2 h at −20 °C, and the color of the solution turned from orange to red. The solvent was removed under reduced pressure at −20 °C. The brownish-red residual solid was rinsed three times with 2 mL of methanol. The solid was dried under reduced pressure, and 0.115 g of **7** was obtained as a red solid (86% yield). $^1H$ NMR (300 MHz, −30 °C, THF-$d_8$): $\delta$ −13.35 (s, 1H, Ru$H$), −11.16 (s, 1H, Ru$H$), −4.78 (s, $J_{Si-H}$ = 60 Hz, 1H, Ru$H$Si), 1.57 (s, 15H, Cp*), 1.63 (s, 15H, Cp*), 7.1−8.3 (m, 20H, Ph). Selective irradiation at each hydride signal at −20 °C did not change the intensities of the other hydride signals. $^{13}$C NMR (125 MHz, −30 °C, THF-$d_8$): $\delta$ 12.3 (q, $J_{C-H} = 126.8$ Hz, $C_5Me_5$), 12.6 (q, $J_{C-H} = 126.8$ Hz, $C_5Me_5$), 86.5 (s, $C_5Me_5$), 96.6 (s, $C_5Me_5$), 114.9 (q, $J_{C-F} = 285.6$ Hz, $CF_3$), 127.1 (d, $J_{C-H} = 160.9$ Hz, Ph), 128.0 (d, $J_{C-H} = 157.7$ Hz, Ph), 128.5 (d, $J_{C-H} = 158.8$ Hz, Ph), 129.0 (d, $J_{C-H} = 157.7$ Hz, Ph), 130.0 (d, $J_{C-H} = 158.7$ Hz, Ph), 130.7 (d, $J_{C-H} = 156.7$ Hz, Ph), 136.0 (d, $J_{C-H} = 157.8$ Hz, Ph), 138.2 (d, $J_{C-H} = 157.7$ Hz, Ph), 146.6 (s, Ph-ipso), 147.4 (s, Ph-ipso), 147.9 (s, Ph-ipso), 148.8 (s, Ph-ipso), 164.3 (q, $^2J_{C-F} = 41.2$ Hz, $COCF_3$). Whereas 16 signals were expected to be observed for the three phenyl groups, only 12 signals can be identified because of the overlap of the signals. $^{29}$Si NMR (54 MHz, −30 °C, toluene-$d_8$): $\delta$ 75.2 (s, $\mu$-$SiPh_2$), 121.7 (d, $J_{Si-H} = 60$ Hz, $\mu$-$\eta^2$-$HSiPh_2$). IR (KBr, cm$^{-1}$): 3062, 2996, 2906, 2058 ($\nu$(RuH)), 1702 ($\nu$(CO)), 1482, 1457, 1430, 1380, 1202 ($\nu$(CF)), 1157, 1096, 1029, 859, 733, 700. Anal. Calcd for $C_{46}H_{53}O_2F_3Ru_2Si_2$: C, 57.95; H, 5.62. Found: C, 57.91; H, 5.47.

**Preparation of $(Cp^*Ru)_2(\mu$-$\eta^2$-$HSiPh_2)(\mu$-$SiPh_2)(\mu$-$CF_3CO_2)(\mu$-$H)(H)$ (7) from Cationic Bis($\mu$-silane) Complex 4a-$BPh_4$.** A 50 mL flask was charged with toluene (20 mL) and $[\{Cp^*Ru(\mu$-$\eta^2$:$\eta^2$-$H_2SiPh_2)\}_2(\mu$-$H)][BPh_4]$ (**4a**-$BPh_4$) (0.104 g, 0.089 mmol). After the reaction flask was cooled to −20 °C, trifluoroacetic acid (7 $\mu$L, 0.093 mmol) was added with vigorous stirring. The solution was allowed to react for 2 h at −20 °C, and the color of the solution turned from yellow to red. The solvent was removed under reduced pressure at −20 °C. The brownish-red residual solid was rinsed three times with 2 mL of methanol. The solid was dried under reduced pressure, and 0.111 g of **7** was obtained as a red solid (86% yield).

**Reaction of $(Cp^*Ru)_2(\mu$-$\eta^2$-$HSiPh_2)(\mu$-$SiPh_2)(\mu$-$CF_3CO_2)(\mu$-$H)(H)$ (7) to 3b in the Presence of Sodium Acetate.** A 50 mL flask was charged with $(Cp^*Ru)_2(\mu$-$\eta^2$-$HSiPh_2)(\mu$-$SiPh_2)(\mu$-$CF_3CO_2)(\mu$-$H)(H)$ (**7**, 0.030 mg, 0.032 mmol) and THF (3 mL). After the reaction flask was cooled at −78 °C with a dry ice/methanol bath, the solution of sodium acetate (0.026 mg, 0.317 mmol) in $H_2O$/acetone (1:2, 3 mL) was added dropwise to the flask. The solution was then slowly warmed to room temperature. The solution became homogeneous at −15 °C. After the solution was allowed to react for 3 h at room temperature, the solvent was removed under reduced pressure. The product was extracted three times with 5 mL of toluene, and the combined extract was passed through Celite on a glass filter. Removal of the solvent in vacuo afforded 28 mg of brownish solid. Formation of **3b** and **3d** was confirmed by the $^1$H NMR spectra of the residual solid, and the yield of **3b** and **3d** was estimated at 87% and 10%, respectively, on the basis of the $^1$H NMR spectra.

**Preparation of $\{Cp^*Ru(\mu$-$H)\}_2\{\mu$-$SiPh(OMe)\}(\mu$-$SiPh_2)$ (3c).** A 50 mL flask was charged with toluene (3 mL) and $\{Cp^*Ru(\mu$-$H)\}_2\{\mu$-$SiPh(OCOCF_3)\}(\mu$-$SiPh_2)$ (**3b**) (0.056 g, 0.063 mmol). Methanol (1 mL) was added with vigorous stirring at 25 °C and allowed to react for 1 h. The solvent was removed under reduced pressure. The brownish-red residual solid was rinsed three times with 2 mL of pentane. The solid was dried under reduced pressure, and 0.029 g of **3c** was obtained as a red solid (58% yield). $^1$H NMR (300 MHz, 25 °C, benzene-$d_6$): $\delta$ −20.08 (br, 2H, Ru*H*), 1.47 (s, 30H, Cp*), 3.35 (s, 3H, O*Me*), 7.1−7.9 (m, 15H, Ph). $^1$H NMR (400 MHz, −60 °C, toluene-$d_8$): $\delta$ −20.35 (d, $J_{H-H} = 5.7$ Hz, 1H, Ru*H*), −19.68 (d, $J_{H-H} = 5.7$ Hz, 1H, Ru*H*), 1.49 (s, 30H, Cp*), 3.33 (s, 3H, O*Me*), 7.1−8.4 (m, 15H, *Ph*). $^{13}$C NMR (75 MHz, 25 °C, benzene-$d_6$): $\delta$ 10.9 (q, $J_{C-H} = 127.2$ Hz, $C_5Me_5$), 51.6 (q, $J_{C-H} = 141.1$ Hz, O*Me*), 90.8 (s, $C_5Me_5$), 136.7 (d, $J_{C-H} = 159.2$ Hz, Ph), 137.6 (d, $J_{C-H} = 157.6$ Hz, Ph), 137.7 (d, $J_{C-H} = 158.2$ Hz, Ph), 145.8 (s, Ph-ipso), 145.9 (s, Ph-ipso), 146.3 (s, Ph-ipso). Whereas 12 signals were expected to be observed for the three phenyl groups, only 6 signals can be identified because of the overlap of the signals and solvent. IR (KBr, cm$^{-1}$): 3058, 2982, 2906, 1582, 1480, 1429, 1383, 1177, 1127, 1091 ($\nu$(SiO)), 1077, 1031, 822, 735, 700.

**Preparation of $Cp^*Ru^+[\eta^6$-$C_6H_5[SiPh(OMe)\{Cp^*Ru^-(H)_2Si(OMe)_2Ph\}]]$ (8).** A 50 mL flask was charged with toluene (3 mL) and $\{Cp^*Ru(\mu$-$H)\}_2\{\mu$-$SiPh(OMe)\}(\mu$-$SiPh_2)$ (**3c**) (0.021 g, 0.026 mmol). Methanol (1 mL) was added with vigorous stirring at 25 °C and allowed to react for 18 h. The solvent was removed under reduced pressure. The product was dissolved in 1 mL of toluene and purified by the use of column chromatography on neutral alumina (Merck Art. 1097) with toluene. Removal of the solvent in vacuo afforded **8** as a white crystalline solid (0.021 g, 95% yield). $^1$H NMR (300 MHz, 25 °C, benzene-$d_6$): $\delta$ −13.90 (s, 1H, Ru*H*), −13.30 (s, 1H, Ru*H*), 1.23 (s, 15H, Cp*), 1.87 (s, 15H, Cp*), 3.40 (s, 3H, OMe), 3.47 (s, 3H, OMe), 4.06 (t, $J_{H-H} = 5.7$ Hz, 1H, $\eta^6$-$C_6H_5Si$), 4.12 (s, 3H, OMe), 4.21 (t, $J_{H-H} = 5.7$ Hz, 1H, $\eta^6$-$C_6H_5Si$), 4.32 (t, $J_{H-H} = 5.7$ Hz, 1H, $\eta^6$-$C_6H_5Si$), 5.54 (d, $J_{H-H} = 5.8$ Hz, 1H, $\eta^6$-$C_6H_5Si$), 5.66 (d, $J_{H-H} = 5.8$ Hz, 1H, $\eta^6$-$C_6H_5Si$), 7.2−8.4 (m, 10H, Ph). $^{13}$C NMR (75 MHz, 25 °C, benzene-$d_6$): $\delta$ 10.3 (q, $J_{C-H} = 128.3$ Hz, $C_5Me_5$), 11.4 (q, $J_{C-H} = 125.6$ Hz, $C_5Me_5$), 49.5 (q, $J_{C-H} = 138.3$ Hz, O*Me*), 49.6 (q, $J_{C-H} = 138.3$ Hz, O*Me*), 53.8 (q, $J_{C-H} = 140.2$ Hz, O*Me*), 84.0 (d, $J_{C-H} = 176.4$ Hz, $\eta^6$-$C_6H_5Si$), 84.1 (d, $J_{C-H} = 173.6$ Hz, $\eta^6$-$C_6H_5Si$), 85.1 (d, $J_{C-H} = 170.7$ Hz, $\eta^6$-$C_6H_5Si$), 88.9 (d, $J_{C-H} = 170.7$ Hz, $\eta^6$-$C_6H_5Si$), 91.6 (d, $J_{C-H} = 176.4$ Hz, $\eta^6$-$C_6H_5Si$), 92.7 (s, $C_5Me_5$), 93.3 (s, $C_5Me_5$), 117.2 (s, $\eta^6$-$C_6H_5Si$-ipso), 135.4 (d, $J_{C-H} = 150.7$ Hz, Ph), 135.7 (d, $J_{C-H} = 159.3$ Hz, Ph), 148.3 (s, Ph-ipso), 148.8 (s, Ph-ipso). Whereas 8 signals were expected to be observed for the two phenyl groups, only 4 signals can be identified because of the overlap of the signals and solvent. IR (KBr, cm$^{-1}$): 3058, 2906, 2812, 1945 ($\nu$(RuH)), 1479, 1381, 1178, 1089, 1029, 698.

**Preparation of $\{Cp^*Ru(\mu$-$H)\}_2\{\mu$-$SiPh(OH)\}(\mu$-$SiPh_2)$ (3d).** A 50 mL flask was charged with dichloromethane (10 mL) and $\{Cp^*Ru(\mu$-$\eta^2$-$HSiPh_2)\}_2(\mu$-$H)(H)$ (**2a**) (0.105 g, 0.13 mmol). The reaction flask was cooled to −78 °C with a dry ice/methanol bath. Trifluoromethanesulfonic acid (13 $\mu$L, 0.14 mmol) was then added to the solution with vigorous stirring. The color of the solution quickly turned from orange to bright yellow. The solution was gently warmed to room temperature and was allowed to react for 10 min at 25 °C, which resulted in exclusive formation of the cationic bis($\mu$-diphenylsilane) complex **4a**-OTf.[2] Alumina (Merck Art. 1097) was then added to the solution, and the color of the solution changed to dark red. The product was extracted three times with 10 mL of dichloromethane, and the combined extract was passed through alumina on a glass filter (Merck Art. 1097). Removal of the solvent in vacuo afforded 0.044 g of **3d** as a brownish-red solid (56% yield). Although the origin of the hydroxy group found in **3d** was not identified, adventitious water on alumina is most likely the source of the hydroxy group. $^1$H NMR (500 MHz, 23 °C, THF-$d_8$): $\delta$ −20.29 (br, 2H, Ru*H*), 1.43 (s, 30H, Cp*), 6.7−8.2 (m, 15H, Ph). $^1$H NMR (500 MHz, −50 °C, THF-$d_8$): $\delta$ −20.50 (d, 1H, $J_{H-H} = 5.8$ Hz, Ru*H*), −20.04 (d, 1H, $J_{H-H} = 5.8$ Hz, Ru*H*), 1.42 (s, 30H, Cp*), 6.9−8.2 (m, 15H, Ph). The resonance for OH was not observed when using THF-$d_8$ as solvent. $^1$H NMR (300 MHz, 23 °C, benzene-$d_6$): $\delta$ −20.03 (br, 2H, Ru*H*), 1.30 (br, 1H, OH), 1.47 (s, 30H, Cp*), 7.1−7.9 (m, 15H, Ph). $^{13}$C{$^1$H} NMR (125 MHz, −50 °C, THF-$d_8$): $\delta$ 11.2 ($C_5Me_5$), 90.8 ($C_5Me_5$), 127.3 (Ph), 127.5 (Ph), 127.8 (Ph), 128.5 (Ph), 129.2 (Ph), 136.9 (Ph), 137.1 (Ph), 137.7 (Ph), 137.9 (Ph), 146.6 (Ph-ipso), 147.2 (Ph-ipso), 147.6 (Ph-ipso). IR (KBr, cm$^{-1}$): 3400 br ($\nu$(OH)), 3048, 2988, 2906, 1479, 1429, 1378, 1121, 1094, 1029, 926, 908, 740, 702.

**Reaction of $\{Cp^*Ru(\mu$-$H)\}_2\{\mu$-$SiPh(OCOCF_3)\}(\mu$-$SiPh_2)$ (3b) with Aqueous KOH.** A 50 mL flask was charged with toluene (4 mL) and $\{Cp^*Ru(\mu$-$H)\}_2\{\mu$-$SiPh(OCOCF_3)\}(\mu$-$SiPh_2)$-(**3b**) (0.036 g, 0.041 mmol). Then 1.0 M aqueous KOH (2 mL, 2.0 mmol) was added to the flask with vigorous stirring. The solution was allowed to react for 12 h at 25 °C. After the solvent was removed under reduced pressure, the residual solid was extracted three times with 10 mL of pentane. The combined extracts were then dried under reduced pressure, and 0.025 mg of residual solid including $\{Cp^*Ru(\mu$-$H)\}_2\{\mu$-

SiPh(OH)}($\mu$-SiPh$_2$) (**3d**), Cp*Ru($\mu$-H)$_4$RuCp* (**1**), and unreacted **3b** was obtained. The yields of **3d** and **1** were estimated at 20 and 9%, respectively, on the basis of the $^1$H NMR spectra of the residual solid.

**Acknowledgment.** This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 14078101, "Reaction Control of Dynamic Complexes") and the 21st Century COE program from the Ministry of Education, Culture, Sports, Science and Technology, Japan. This research was also supported by fellowships of the Japan Society for the Promotion of Science for Japanese Junior Scientists. We acknowledge Kanto Chemical Co., Inc., for generous gifts of pentamethylcyclopentadiene and several kinds of silanes.

**Supporting Information Available:** Tables of atomic coordinates and thermal parameters, bond lengths and angles, torsion angles, and structure refinement details and ORTEP drawings of **2c** and **8** with full numbering schemes. Parameters for the dynamic NMR simulations of **3b**–**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049328H