

$\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -Coordination of Primary Silane on a Triruthenium Plane

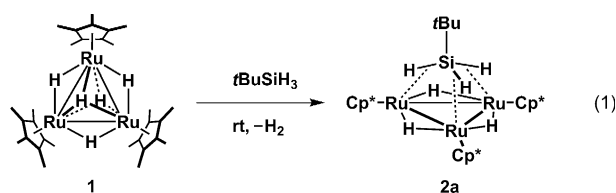
Masahiro Nagaoka, Hiroyuki Tsuruda, Masa-aki Amako, Hiroharu Suzuki, and Toshiro Takao*

Abstract: A $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -silane complex, $[(\text{Cp}^*\text{Ru})_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-H}_3\text{Si}t\text{Bu})(\mu\text{-H})_3]$ (**2a**; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), was synthesized from the reaction of $[(\text{Cp}^*\text{Ru}(\mu\text{-H}))_3(\mu_3\text{-H})_2]$ (**1**) with $t\text{BuSiH}_3$. Complex **2a** is the first example of a silane ligand adopting a $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ coordination mode. This unprecedented coordination mode was established by NMR and IR spectroscopy as well as X-ray diffraction analysis and supported by a density functional study. Variable-temperature NMR analysis implied that **2a** equilibrates with a tautomeric μ_3 -silyl complex (**3a**). Although **3a** was not isolated, the corresponding μ_3 -silyl complex, $[(\text{Cp}^*\text{Ru})_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-H}_2\text{SiPh})(\text{H})(\mu\text{-H})_3]$ (**3b**), was obtained from the reaction of **1** with PhSiH_3 . Treatment of **2a** with PhSiH_3 resulted in a silane exchange reaction, leading to the formation of **3b** accompanied by the elimination of $t\text{BuSiH}_3$. This result indicates that the μ_3 -silane complex can be regarded as an “arrested” intermediate for the oxidative addition/reductive elimination of a primary silane to a trinuclear site.

Since Kubas discovered the first $\eta^2\text{-H}_2$ complex,^[1] the significant importance of σ -complexation of H–H and C–H bonds has been widely recognized, in particular in the bond activation step. To date, many complexes containing an $\eta^2\text{-H}_2$ ligand have been synthesized, and the nature of the σ -bonding to a transition-metal center is unambiguously established.^[2] An Si–H bond has also been shown to coordinate to a metal center, while retaining an Si–H interaction;^[3] these are often referred to as σ -complexes. The two Si–H bonds of a secondary silane can bind to a dinuclear center via σ -coordination, yielding a $\mu\text{-}\eta^2\text{:}\eta^2$ -silane complex.^[4] μ -Silane complexes are regarded as “arrested” intermediates of successive oxidative additions of secondary silanes to a dinuclear center. Its trinuclear analogue, however, has never been synthesized before, although it could be the initial stage of multimetallic activation of primary silanes on a trinuclear site.

We recently synthesized heterometallic trinuclear complexes of Ru and Group 9 metals having a $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -silyl ligand, $[(\text{Cp}^*\text{Ru})_2(\text{Cp}^*\text{M})(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-H}_2\text{SiR})(\mu\text{-H})_3]$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$; $\text{R} = t\text{Bu}, \text{Ph}$).^[5] These μ_3 -silyl ligands exhibited a dynamic behavior, leading to the site-exchange of hydrides and agostic

Si–H bonds. A $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -silane complex has been postulated as a suitable intermediate for the site-exchange despite the lack of spectroscopic evidence. A $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -coordination of primary silanes is not only the initial stage of the reaction on a trinuclear site, but it could also be an appropriate model for the chemisorption of primary silanes on a metal surface. Herein, we report the synthesis of a novel $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -silane complex from the reaction of the triruthenium complex, $[(\text{Cp}^*\text{Ru}(\mu\text{-H}))_3(\mu_3\text{-H})_2]$ (**1**), with $t\text{BuSiH}_3$. This is in contrast to the reaction of **1** with PhSiH_3 , which led to the formation of a $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -silyl complex.



Complex **1** reacted with $t\text{BuSiH}_3$ at 25 °C to yield a triply bridging silane complex, $[(\text{Cp}^*\text{Ru})_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-H}_3\text{Si}t\text{Bu})(\mu\text{-H})_3]$ (**2a**) [Eq. (1)]. A singlet at $\delta = 4.48$ ppm appears in the ^1H NMR spectrum of a reaction performed in a sealed NMR tube, which clearly shows the elimination of dihydrogen from the triruthenium site. Although $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ coordination of a borohydrido ligand in trinuclear Ru^[6] and Fe complexes^[7] through 3c–2e M–H–B interactions is known, to the best of our knowledge, **2a** is the first example of Group 14 elements adopting a $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ coordination mode. This unprecedented $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -silane structure was confirmed by NMR and IR data, as well as X-ray diffraction (XRD) analysis.

The XRD analysis of **2a** was carried out using a single crystal obtained from a cold pentane solution.^[8] Although there were two independent molecules, **2a** and **2a'**, exhibiting similar geometric parameters in the asymmetric unit, only **2a** is shown in Figure 1. The triruthenium plane forms an isosceles triangle (Ru1–Ru2 2.9827(6) Å, Ru2–Ru3 2.9764(5) Å, Ru1–Ru3 3.0530(5) Å). While the Ru3–Si1 bond (2.4163(14) Å) is slightly lengthened compared to the Ru1–Si1 (2.3697(14) Å) and Ru2–Si1 bond (2.3335(15) Å), which is most likely due to Jahn–Teller distortion, these lie in the reported range for the Ru–Si distances forming Ru–H–Si interactions (2.167–2.675 Å).^[9] Owing to the steric repulsion between the $t\text{Bu}$ group and the Cp^* groups, all of the Cp^* groups are directed in the opposite face of the μ_3 -silane ligand with respect to the Ru_3 plane. Although the positions of the hydrido ligands were not determined, density functional theory (DFT) calculations on **2a** demonstrated that three of the hydrido ligands bridge the Ru–Si bonds, forming 3c–2e Ru–H–Si interactions, while the other three hydrides bridge

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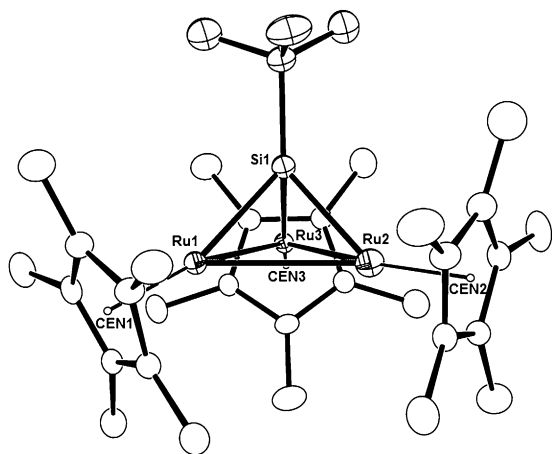


Figure 1. Molecular structure and labeling of **2a** with ellipsoids set at 30% probability. Selected distances [Å] and angles [°]: Ru1–Ru2 2.9827(6), Ru2–Ru3 2.9764(5), Ru1–Ru3 3.0530(5), Ru1–Si1 2.3697(14), Ru2–Si1 2.3335(15), Ru3–Si1 2.4163(14); Ru2–Ru1–Ru3 59.079(12), Ru1–Ru2–Ru3 61.639(13), Ru1–Ru3–Ru2 59.282(13).

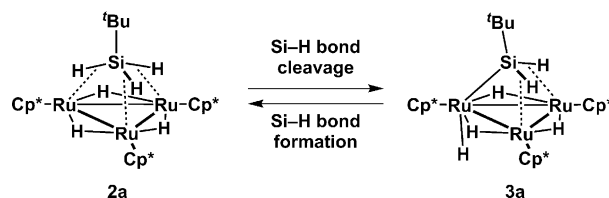
the Ru–Ru edges (Supporting Information, Figure S15). Furthermore, Wiberg bond indices for the Si–H bonds (0.4340, 0.3209, 0.2640) indicated that *t*BuSiH₃ coordinates to the triruthenium plane while maintaining a bonding interactions between Si and H atoms. While silyl ligands bound to a metal center through three or more M–H–Si interactions have been elucidated by several groups,^[10] to the best of our knowledge, **2a** is the first trinuclear example, in which the central silicon ligand is coordinated to a M₃ center through the three Si–H bonds of primary silane.

The σ-coordination of the Si–H bond was also confirmed by means of IR spectroscopy. In the IR spectrum of **2a**, while $\nu(\text{Ru–H–Ru})$ was not detected,^[11] a broad and intense band assignable to $\nu(\text{Ru–H–Si})$ was observed at 1888 cm^{−1}. The lack of sharp adsorption around 2000 cm^{−1} clearly showed that **2a** possesses neither Ru–H nor non-coordinated Si–H bonds, which usually appear in the range of 2000–2100 cm^{−1} as a sharp and intense peak.^[4a,12] Although the red-shift upon deuteration was not clearly seen in the differential spectrum, the broad band disappeared in the IR spectrum of [(Cp*₃Ru)₃(μ₃-η²:η²:η²-D₃Si*t*Bu)(μ-D)₃] ([D₆]-**2a**; Supporting Information, Figure S12). This indicates that the absorption observed at 1888 cm^{−1} in the IR spectrum of **2a** is derived from $\nu(\text{Ru–H–Si})$.

In the ¹H NMR spectrum of **2a** recorded at −100 °C, only one sharp signal at $\delta = -16.81$ ppm was observed for the hydrides. This indicated that the hydrides undergo rapid site-exchange within the NMR timescale. Satellite peaks were observed with an apparent $J_{\text{Si,H}}$ value of 21 Hz. Since the coupling constant must be an average of the six $J_{\text{Si,H}}$ values owing to the site-exchange, the true $J_{\text{Si,H}}$ value for Ru–H–Si can be estimated to be about 42 Hz.^[13] This lies in the reported range for η²-Si–H bonds (20–140 Hz).^[3a]

The signal for the Cp* groups was observed to be equivalent and resonated at $\delta = 1.94$ ppm at −100 °C. Although the shape of the Cp* signal did not change at 20 °C, the hydride signal became broader with elevating temperatures, and underwent a noticeable downfield shift of

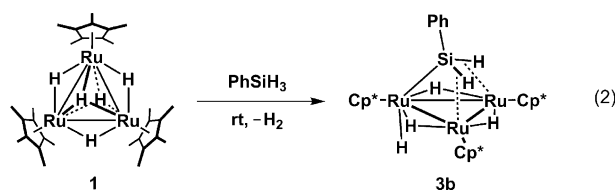
0.15 ppm (Supporting Information, Figure S9). This spectral change can probably be ascribed to the equilibrium between **2a** and the tautomeric μ₃-η²:η²-silyl complex, [(Cp*₃Ru)₃(μ₃-η²:η²-H₂Si*t*Bu)(μ-H)₃(H)] (**3a**), which was formed via Si–H bond cleavage (Scheme 1). The formal oxidation state of **2** can be estimated at (II, II, II). Since **3** was formed by



Scheme 1. Equilibrium between **2a** and **3a** via Si–H bond cleavage/formation.

oxidative addition of one of the Si–H bonds in **2**, the oxidation state of **3** is formally increased by 2 and becomes (IV, II, II). A similar equilibrium, which involves reversible B–H bond cleavage/formation, was also observed in the μ₃-η²:η²:η²-borohydrido complex, [Ru₃(CO)₉(μ₃-η²:η²:η²-H₃BH)].^[6]

Although no spectral and structural data were obtained for **3a**, μ₃-η²:η²-silyl complex **3b** was exclusively obtained from the reaction of **1** with PhSiH₃ [Eq. (2)]. Unlike the ¹H NMR spectrum of **2a**, the ¹H NMR spectrum of **3b** recorded at −120 °C showed four broad hydride signals resonating at $\delta = -21.09$, −19.08, −13.29, and −11.56 ppm with an intensity ratio of 1:2:1:2 (Supporting Information, Figure S10). The four broad hydride signals coalesced at −100 °C, and resonated at $\delta = -15.86$ ppm at −30 °C as a sharp singlet. At −120 °C, the signals derived from the Cp* groups broaden and were buried under the baseline, while they coalesced and appeared as a sharp singlet at −30 °C. These spectral features observed at −120 °C are consistent with the μ₃-silyl structure in **3b** exhibiting a non-crystallographic C_s symmetry. These spectral change suggest that the hydrides in **3b** undergo rapid site-exchange, which is most likely via the formation of the μ₃-silane intermediate **2b** as shown in Scheme 1.



The μ₃-silyl structure of **3b** is confirmed by the presence of a terminal Ru–H, which was detected as a sharp absorption at 1931 cm^{−1} in the IR spectrum. Along with the $\nu(\text{Ru–H})$ mode, a broad absorption assignable to $\nu(\text{Ru–H–Si})$ was also observed at around 1790 cm^{−1}.

The ²⁹Si signal of **3b** recorded at ambient temperature appeared at $\delta = 194.2$ ppm. This appeared at a considerably

lower magnetic field in comparison with that of the μ_3 -silane complex **2a** ($\delta = 175.5$ ppm). Although the ^{29}Si signal of free PhSiH_3 ($\delta = -59.8$ ppm) appears at a higher magnetic field than that of $t\text{BuSiH}_3$ ($\delta = -39.8$ ppm), the ^{29}Si signal of **3b** appeared at a lower magnetic field than that of **2a** after complexation to the triruthenium core. This opposite trend would be due to the difference of the coordination modes in these complexes, while conclusive evidence does not come from only chemical shifts because the signal of ^{29}Si appears over a wide range.^[3b,c]

The molecular structure of **3b** was determined by XRD analysis, as shown in Figure 2. The positions of the hydrido ligands were successfully determined using Fourier synthesis, which agreed with the NMR and IR data. Unlike the

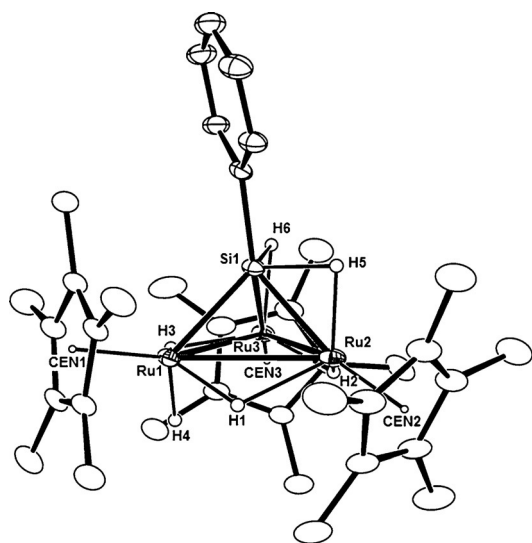


Figure 2. Molecular structure and labeling of **3b** with ellipsoids set at 30% probability. Selected distances [Å] and angles [°]: Ru1–Ru2 3.0009(5), Ru2–Ru3 3.0956(5), Ru1–Ru3 3.9988(5), Ru1–Si1 2.3394(13), Ru2–Si1 2.3561(13), Ru3–Si1 2.3759(12); Ru2–Ru1–Ru3 62.123(12), Ru1–Ru2–Ru3 58.906(12), Ru1–Ru3–Ru2 58.971(12).

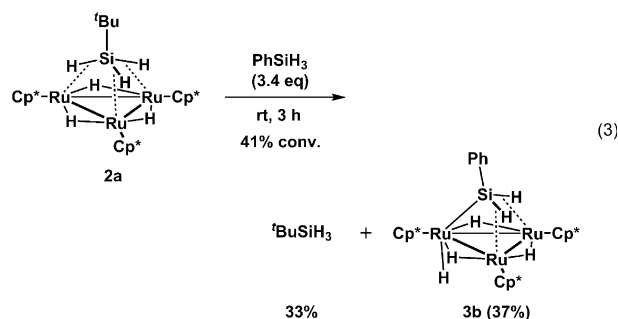
molecular structure of **2a**, one of the Cp* groups attached to the Ru1 atom bent upwards with respect to the Ru_3 plane. This is probably due to the presence of the terminal hydride, H4, at Ru1. Although no significant difference was observed between the Ru–Si distances (Ru1–Si1 2.3394(13) Å, Ru2–Si1 2.3561(13) Å, Ru3–Si1 2.3759(12) Å), the orientation of the Cp* at Ru1 strongly indicates that oxidative addition of the Si–H bond occurred at Ru1.

While the reaction of **1** with $t\text{BuSiH}_3$ afforded μ_3 -silane complex **2a**, μ_3 -silyl complex **3b** was obtained from the reaction of **1** with PhSiH_3 . To gain insight into the stability of μ_3 -silane complex **2** and μ_3 -silyl complex **3**, DFT calculations on **2a,b** and **3a,b** were examined. The calculated structures and important geometrical parameters are listed in the Supporting Information, Tables S3 and S7. The optimized structures for **2a** and **3b** are in a reasonable agreement with the results from XRD analyses. Although experimental data are insufficient, the calculations provided plausible structures for **2b** and **3a**. The Gibbs energies of **2a** and **3a** show that **2a**

is slightly more stable than **3a** by 0.13 kcal mol^{−1} at 298 K. On the other hand, **3b** is more stable than **2b** by 4.94 kcal mol^{−1}. This opposite trend of the stabilities are consistent with the fact that **2a** and **3b** were major isomers.

It has been known that oxidative addition of an Si–H bond occurred readily when it possesses an electron-withdrawing substituent because of its lower $\sigma^*(\text{Si–H})$ level.^[14] Thus, the preference of PhSiH_3 to **3** can be rationalized by the electronic factors. Furthermore, the steric repulsion between the substituent and the Cp* groups also appear to dominate the thermodynamic stability of **2** and **3**. In the optimized structure of **3**, one of the Cp* groups bends upwards with respect to the Ru_3 plane and is directed to the same side as the Si atom. When the Si atom possesses a bulky $t\text{Bu}$ group, **3a** becomes unstable owing to the steric repulsion between the $t\text{Bu}$ group and the Cp* groups. Therefore, all of the Cp* groups bend towards the other side of the Si atom with respect to the Ru_3 plane, and form **2a**. In contrast, when the Si atom contains a smaller phenyl group, the μ_3 -silyl structure is favored over the μ_3 -silane form.

Fehlner and co-workers demonstrated the related equilibrium in $[\text{Fe}_3(\text{CO})_9(\text{CH}_4)]$, namely the equilibrium among μ_3 -methylidyne, μ_3 -methylene, and μ -methyl complexes.^[15] However, a μ_3 -methane complex was not observed. The equilibrium between μ_3 -silyl complex **3** and μ_3 -silane complex **2** via reversible Si–H bond formation/scission implies that the μ_3 -silane complex could be an intermediate of the elimination of a primary silane from a trinuclear site. In fact, treatment of **2a** with 3.4 equiv PhSiH_3 resulted in a silane-exchange reaction, namely the formation of **3b** accompanied by the liberation of $t\text{BuSiH}_3$ [Eq. (3)].



On the other hand, **3b** did not react even with a large excess amount of $t\text{BuSiH}_3$, and PhSiH_3 was not eliminated from the Ru_3 plane. While several silane exchange reactions controlled by the electronic^[16] and steric factors^[17] have been elucidated for monometallic silyl complexes, this thermodynamic preference implies that PhSiH_3 interacts with the Ru_3 center stronger than $t\text{BuSiH}_3$, which is probably due to the preference for the μ_3 -silyl complex.

We previously reported the reaction of **1** with linear alkanes leading to the formation of the *closo*-ruthenacyclopentadiene complex, and demonstrated the mechanism of the skeletal rearrangement performed on the Ru_3 plane.^[18] However, the initial stage of the reaction, namely the incorporation of an alkane into the Ru_3 plane, is still

unknown. The $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -silane complex could be a suitable model for the initial stage of alkane activation by a trinuclear complex.

In summary, an unprecedented μ_3 -silane complex **2a** was synthesized from the reaction of **1** with $t\text{BuSiH}_3$, and its unique $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -coordination mode was established by NMR and IR data as well as an XRD analysis. The spectral change in the ^1H NMR spectra implies that **2a** equilibrates with the tautomeric μ_3 -silyl complex **3a** via oxidative addition of an Si–H bond. While the formation of **3a** was not directly observed, **3b** was exclusively prepared by the reaction of **1** with PhSiH_3 . As for other σ -complexes, the μ_3 -silane complex can be regarded as an arrested intermediate of oxidative addition to the trinuclear site. Moreover, it could be a model for the chemisorption of saturated compounds on a metal surface.

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- [1] G. J. Kubas, R. R. Ryan, D. J. Wroblewski, *J. Am. Chem. Soc.* **1984**, *106*, 451–452.
- [2] G. J. Kubas, *Metal Dihydrogen and σ -Bond Complexes*, Kluwer/Plenum, New York, **2001**.
- [3] a) U. Schubert, *Adv. Organomet. Chem.* **1990**, *30*, 151–187; b) J. Y. Corey, *Chem. Rev.* **2011**, *111*, 863–1071; c) J. Y. Corey, J. Braddock-Wilking, *Chem. Rev.* **1999**, *99*, 175–292.
- [4] a) T. Takao, S. Yoshida, H. Suzuki, M. Tanaka, *Organometallics* **1995**, *14*, 3855–3868; b) Y. Ohki, T. Kojima, M. Oshima, H. Suzuki, *Organometallics* **2001**, *20*, 2654–2656; c) M. Tanabe, D. Ito, K. Osakada, *Organometallics* **2007**, *26*, 459–462; d) M. A. Alvarez, M. P. Alvarez, R. Carreño, M. A. Ruiz, C. Bois, *J. Organomet. Chem.* **2011**, *696*, 1736–1748; e) Z. M. Heiden, G. Zampella, L. D. Gioia, T. B. Rauchfuss, *Angew. Chem. Int. Ed.* **2008**, *47*, 9756–9759; *Angew. Chem.* **2008**, *120*, 9902–9905; f) T. Takao, S. Yoshida, H. Suzuki, *Chem. Lett.* **2001**, 1100–1101; g) J. Hoyano, M. Elder, W. A. G. Graham, *J. Am. Chem. Soc.* **1969**, *91*, 4568–4569; h) H. Hashimoto, Y. Hayashi, I. Aratani, C. Kabuto, M. Kira, *Organometallics* **2002**, *21*, 1534–1536.
- [5] M. Nagaoka, T. Shima, T. Takao, H. Suzuki, *Organometallics* **2014**, *33*, 7232–7240.
- [6] J. C. Vites, C. Eigenbrot, T. P. Fehlner, *J. Am. Chem. Soc.* **1984**, *106*, 4633–4635.
- [7] A. K. Chipperfield, C. E. Housecroft, *J. Organomet. Chem.* **1988**, *349*, C17–C21.
- [8] CCDC 1413579 (**2a**) and 1413580 (**3b**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.
- [9] Structural data for 34 complexes having Ru–H–Si interaction(s) were obtained from Cambridge Structural Database System Version 5.36 (November 2014 plus one update): F. A. Allen, *Acta Crystallogr. Sect. B* **2002**, *58*, 380–388.
- [10] a) N. M. Yardy, F. R. Lemke, L. Brammer, *Organometallics* **2001**, *20*, 5670–5674; b) M. C. Lipke, T. D. Tilley, *J. Am. Chem. Soc.* **2011**, *133*, 16374–16377; c) R. B. Said, K. Hussein, J.-C. Barthelat, I. Atheaux, S. Sabo-Etienne, M. Grellier, B. Donnadieu, B. Chaudret, *Dalton Trans.* **2003**, 4139–4146; d) I. Atheaux, B. Donnadieu, V. Rodriguez, S. Sabo-Etienne, B. Chaudret, K. Hussein, J.-C. Barthelat, *J. Am. Chem. Soc.* **2000**, *122*, 5664–5665; e) M. C. Lipke, T. D. Tilley, *Angew. Chem. Int. Ed.* **2012**, *51*, 11115–11121; *Angew. Chem.* **2012**, *124*, 11277–11283.
- [11] a) H. D. Kaesz, R. B. Saillant, *Chem. Rev.* **1972**, *72*, 231–281; b) D. S. Moore, S. D. Robinson, *Chem. Soc. Rev.* **1983**, *12*, 415–452.
- [12] S. Lachaize, S. Sabo-Etienne, *Eur. J. Inorg. Chem.* **2006**, 2115–2127.
- [13] We assume that the $^2J_{\text{Si,H}}$ value between the μ_3 -Si ligand and Ru–H–Ru is close to 0 Hz. Since the rapid site-exchange between these sites should average the $J_{\text{Si,H}}$ values, the $^1J_{\text{Si,H}}$ in Ru–H–Si can be estimated at 42 Hz.
- [14] a) D. L. Lichtenberger, A. Rai-Chaudhuri, *J. Am. Chem. Soc.* **1989**, *111*, 3583–3591; b) D. L. Lichtenberger, A. Rai-Chaudhuri, *Inorg. Chem.* **1990**, *29*, 975–981; c) D. L. Lichtenberger, A. Rai-Chaudhuri, *J. Am. Chem. Soc.* **1990**, *112*, 2492–2497.
- [15] a) J. C. Vites, G. Jacobsen, T. K. Dutta, T. P. Fehlner, *J. Am. Chem. Soc.* **1985**, *107*, 5563–5565; b) T. K. Dutta, J. C. Vites, G. B. Jacobsen, T. P. Fehlner, *Organometallics* **1987**, *6*, 842–8447.
- [16] K. Osakada, S. Sarai, T. Koizumi, T. Yamamoto, *Organometallics* **1997**, *16*, 3973–3980.
- [17] a) V. K. Dioumaev, L. J. Procopio, P. J. Carroll, D. H. Berry, *J. Am. Chem. Soc.* **2003**, *125*, 8043–8058; b) D. Chan, S. B. Duckett, S. L. Heath, I. G. Khazal, R. N. Perutz, S. Sabo-Etienne, P. L. Timmins, *Organometallics* **2004**, *23*, 5744–5756; c) J. L. McBee, J. Escalada, T. D. Tilley, *J. Am. Chem. Soc.* **2009**, *131*, 12703–12713; d) A. Y. Khalimon, S. K. Ignatov, A. I. Okhupkin, R. Simionescu, L. G. Kuzmina, J. A. K. Howard, G. I. Nikonov, *Chem. Eur. J.* **2013**, *19*, 8573–8590.
- [18] T. Takao, H. Suzuki, *Bull. Chem. Soc. Jpn.* **2014**, *87*, 443–458.

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