2200 *Organometallics* **1997,** *16,* 2200−2203

Reactivity of a Donor-Stabilized Bis(silylene)ruthenium Complex toward Nucleophiles ROH (R = Me, H)

Hiroaki Wada, Hiromi Tobita,* and Hiroshi Ogino*

Department of Chemistry, Graduate School of Science, Tohoku University,
Sendai 980-77, Japan

Received December 6, 1996[⊗]

The reaction of the bis(silylene)ruthenium complex Cp(Ph$_3$P)Ru{SiMe$_2$···O(Me)···SiMe$_2$} (**1**) with MeOH afforded *trans*-Cp(Ph$_3$P)RuH(SiMe$_2$OMe)$_2$ (**2**). Complex **2** reacted further slowly with an excess of MeOH to give *trans*-Cp(Ph$_3$P)Ru(H)$_2$(SiMe$_2$OMe) (**3**) and Me$_2$Si(OMe)$_2$. In contrast, the reaction of **1** with H$_2$O yielded first the metallacycle Cp(Ph$_3$P)$\overline{\mathrm{RuH(SiMe_2OSi}}\mathrm{Me_2)}$ (**4**), which then was converted to the tetrasiloxane complex [Cp(Ph$_3$P)Ru(H)$_2$SiMe$_2$OSiMe$_2$]$_2$O (**5**) by the action of an excess of H$_2$O.

Introduction

Silylene complexes which contain silicon−transition-metal unsaturated bonds are important intermediates in metal-catalyzed transformations of organosilicon compounds,[1] so that studies of the reactivity of isolated silylene complexes could provide useful information on the mechanisms of such reactions. Many reactions of silylene complexes have been reported,[2−8] but most are accompanied by subsequent reactions: cleavage of silicon−metal bonds, thermal or photochemical silylene dissociation,[2−4] and nucleophilic substitution on the silicon atom by alcohols,[3,4] ketones,[2b,4] or H$_2$O.[3c] The only exceptions are the reactions of bis(silylene)iron complexes[5] and intramolecularly amino-stabilized silylene complexes[6,7] with alcohols or water, that give addition products in which the silicon−metal bonds are retained. However, reactions involving simple addition to a silicon−metal multiple bond are rare. Several MO calculations on silylene complexes suggested that the silicon−metal double bond is strongly polarized ($\mathrm{Si}^{\delta+}{=}\mathrm{M}^{\delta-}$), and therefore, the silicon atom is expected to be vulnerable to nucleophilic attack.[2b,9,10] Thus, addition of nucleophiles to the silicon−metal double bond should be one of the most common reactions of silylene complexes.

Previously, we reported the synthesis and structure of the methoxy-bridged bis(silylene)ruthenium complex Cp(Ph$_3$P)Ru{SiMe$_2$···O(Me)···SiMe$_2$} (Cp = η^5-C$_5$H$_5$) (**1**).[11] We now report the reactions of **1** with ROH (R = Me, H) nucleophiles, which give first nucleophilic addition products that then are attacked by nucleophiles to give slowly products of silicon−metal bond cleavage.

Experimental Section

All manipulations were performed using Schlenk tube techniques under a nitrogen atmosphere. Benzene, pentane, and DME (1,2-dimethoxyethane) were distilled from a potassium mirror. MeOH was distilled from magnesium. Me$_2$Si(OMe)$_2$ was prepared by the reaction of Me$_2$SiCl$_2$ and MeOH in the presence of (H$_2$N)$_2$CO as HCl acceptor. Cp(Ph$_3$P)Ru{SiMe$_2$···O(Me)···SiMe$_2$} (**1**)[11] and Cp(Ph$_3$P)$_2$RuMe[12] were prepared by reported methods. HSiMe$_2$OSiMe$_2$H was obtained from Shin-Etsu Chemical Co., Ltd., and distilled from P$_2$O$_5$. NMR spectra were recorded on Bruker ARX-300 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz; ^{31}P, 122 MHz) and JEOL FX-90Q (^{31}P, 36.3 MHz) spectrometers. IR spectra were recorded on a Horiba FT-200 spectrophotometer. Mass spectra were recorded on JEOL JMS-HX110 and Hitachi M-2500S mass spectrometers.

***trans*-Cp(Ph$_3$P)Ru(H)(SiMe$_2$OMe)$_2$ (2).** Complex **1** (63.4 mg, 110 μmol) was placed in a Schlenk tube and dissolved in benzene (2.5 mL). MeOH (10 mL, 0.24 mmol) was added to the solution at room temperature, and the volatiles were removed immediately after the addition. The yellow oily residue was dissolved in pentane (0.8 mL) and cooled to −94 °C. After a yellow precipitate had formed, the supernatant liquid was removed by syringe and the precipitate was washed with 0.5 mL of pentane and dried under vacuum to give *trans*-Cp(Ph$_3$P)Ru(H)(SiMe$_2$OMe)$_2$ (**2**) as a yellow powder (55.8 mg, 91.7 μmol, yield 83%). Spectral data for **2**: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ −11.95 (1H, d, $^2J_{\mathrm{H-P}}$ = 10.1 Hz, RuH), 0.38 (6H, s, SiMe), 0.42 (6H, s, SiMe), 3.25 (6H, s, OMe), 4.73 (5H, s, Cp), 7.04−7.69 (15H, m, Ph$_3$P); ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ 10.0 (s, SiMe), 11.2 (s, SiMe), 50.2 (s, OMe), 86.7 (s, Cp), 127.6 (d, $J_{\mathrm{C-P}}$ = 9.1 Hz, Ph$_3$P), 128.1 (d, $J_{\mathrm{C-P}}$ = 1.5 Hz, Ph$_3$P), 128.4 (d,

---

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1997.

(1) (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24, p 1415. (b) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Chapters 9 and 10, pp 245, 309.

(2) (a) Zybill, C.; Wilkinson, D. L.; Leis, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 203. (b) Leis, C.; Wilkinson, D. L.; Handwerker, H.; Zybill, C. *Organometallics* **1992**, *11*, 514.

(3) (a) Corriu, R. J. P.; Lanneau, G. F.; Chauhan, B. P. S. *Organometallics* **1993**, *12*, 2001. (b) Corriu, R. J. P.; Chauhan, B. P. S.; Lanneau, G. F. *Organometallics* **1995**, *14*, 1646. (c) Chauhan, B. P. S.; Corriu, R. J. P.; Lanneau, G. F.; Priou, C. *Organometallics* **1995**, *14*, 1657.

(4) Zhang, C.; Grumbine, S. D.; Tilley, T. D. *Polyhedron* **1991**, *10*, 1173.

(5) Ueno, K.; Tobita, H.; Seki, S.; Ogino, H. *Chem. Lett.* **1993**, 1723.

(6) Handwerker, H.; Leis, C.; Probst, R.; Bissinger, P.; Grohmann, A.; Kiprof, P.; Herdtweck, E.; Blümel, J.; Auner, N.; Zybill, C. *Organometallics* **1993**, *12*, 2162.

(7) Kobayashi, H.; Ueno, K.; Ogino, H.; *Organometallics* **1995**, *14*, 5490.

(8) Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 6951.

(9) (a) Nakatsuji, H.; Ushio, J.; Yonezawa, T. *J. Organomet. Chem.* **1983**, *258*, C1. (b) Cundari, T. R.; Gordon, M. S. *J. Phys. Chem.* **1992**, *96*, 631. (c) Márquez, A.; Sanz, F. *J. Am. Chem. Soc.* **1992**, *114*, 2903. (d) Jacobsen, H.; Ziegler, T. *Organometallics* **1995**, *14*, 224. (e) Jacobsen, H.; Ziegler, T. *Inorg. Chem.* **1996**, *35*, 775.

(10) (a) Zybill, C.; Müller, G. *Organometallics* **1988**, *7*, 1368. (b) Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 5495.

(11) Tobita, H.; Wada, H.; Ueno, K.; Ogino, H. *Organometallics* **1994**, *13*, 2545.

(12) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2376.

S0276-7333(96)01031-X CCC: $14.00

J_{C-P} = 39.2 Hz, Ph_3P), 134.3 (d, J_{C-P} = 9.6 Hz, Ph_3P); ^{29}Si NMR (59.6 MHz, C_6D_6) δ 51.1 (d, $^2J_{C-P}$ = 11.6 Hz); ^{31}P NMR (36.3 MHz, C_6D_6) δ 57.0 (s); IR (hexane solution) 1994 (RuH), 1238 (SiMe), 1182, 1090 (SiOMe) cm^{-1}; MS (EI, 70 eV) *m/z* 577 (2.0, $M^+ -$ OMe), 562 (9.4, $M^+ -$ Me $-$ OMe), 546 (1.7, $M^+ -$ 2(OMe)), 531 (1.2, $M^+ -$ 2(OMe) $-$ Me), 429 (100, [Cp(Ph$_3$P)Ru]$^+$), 262 (91, (PPh$_3$)$^+$), 89 (8.0, (SiMe$_2$OMe)$^+$). Anal. Calcd for $C_{29}H_{39}O_2PRuSi_2$: C, 57.30; H, 6.47. Found: C, 57.59; H, 6.41.

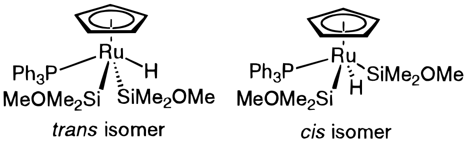
***trans*-Cp(Ph$_3$P)Ru(H)$_2$(SiMe$_2$OMe) (3).** Toluene (2 mL) and MeOH (80 μL, 2.0 mmol) were transferred to a Pyrex tube (20 mm o.d.) containing complex **1** (111 mg, 193 μmol) and a stirbar by the trap-to-trap-transfer technique under high vacuum, and the tube was flame-sealed. After 72 h of stirring at room temperature, the tube was opened in the glovebox, the solution was transferred into a Schlenk tube, and the volatiles were removed under reduced pressure. The orange residue was dissolved in pentane (2 mL) and cooled to -98 °C. After a yellow precipitate had formed, the supernatant liquid was removed by syringe and the precipitate was washed with 1 mL of pentane twice; drying under vacuum gave *trans*-Cp(Ph$_3$P)Ru(H)$_2$(SiMe$_2$OMe) (**3**; 58.7 mg, 113 μmol, yield 59%) as an orange oil. Spectral data for **3**: ^{1}H NMR (300 MHz, toluene-d_8) δ -11.87 (2H, d, $^2J_{H-P}$ = 26.8 Hz, RuH), 0.34 (6H, s, SiMe), 3.36 (3H, s, OMe), 4.64 (5H, s, Cp), 6.99$-$7.62 (15H, m, Ph$_3$P); ^{13}C NMR (75.5 MHz, toluene-d_8) δ 12.7 (s, SiMe), 49.9 (s, OMe), 84.1 (s, Cp), 127.8 (d, J_{C-P} = 9.8 Hz, Ph$_3$P), 129.3 (d, J_{C-P} = 2.3 Hz, Ph$_3$P), 134.0 (d, J_{C-P} = 11.2 Hz, Ph$_3$P), 140.4 (d, J_{C-P} = 45.8 Hz, Ph$_3$P); ^{29}Si NMR (59.6 MHz, toluene-d_8) δ 51.1 (d, $^2J_{Si-P}$ = 10.0 Hz); ^{31}P NMR (122 MHz, toluene-d_8) δ 71.4 (s); IR (hexane solution) 1971 (RuH), 1238 (SiMe), 1184, 1093 (SiOMe) cm^{-1}; MS (EI, 70 eV) *m/z* 520 (2.1, M$^+$), 505 (3.2, $M^+ -$ Me), 488 (3.2, $M^+ -$ OMe $-$ H), 429 (100, [Cp(Ph$_3$P)Ru]$^+$), 262 (9.1, (PPh$_3$)$^+$); exact mass calcd for $C_{26}H_{31}OPRuSi$ 520.0926, found 520.0928.

Cp(Ph$_3$P)Ru(H)(SiMe$_2$OSiMe$_2$) (4). Complex **1** (65.0 mg, 113 μmol) was dissolved in DME (10 mL), and H$_2$O (6 μL, 0.3 mmol, 3 equiv) was added at room temperature. Immediately after the addition, volatiles were removed to give a yellow oily residue. The residue was dissolved in hexane (1 mL), and the solution was cooled to -94 °C to form a yellow precipitate. On removal of the supernatant liquid followed by washing with pentane (0.5 mL), Cp(Ph$_3$P)Ru(H)(SiMe$_2$OSiMe$_2$) (**4**) was obtained as a yellow powder (50.7 mg, 90.3 μmol, yield 80%). Spectral data for **4**: ^{1}H NMR (300 MHz, C_6D_6) δ -11.68 (1H, d, $^2J_{H-P}$ = 26.6 Hz, RuH), 0.21 (3H, s, SiMe), 0.56 (3H, s, SiMe), 0.70 (3H, s, SiMe), 0.78 (3H, s, SiMe), 4.56 (5H, s, Cp), 7.00$-$7.70 (15H, m, PPh$_3$); ^{13}C NMR (75.5 MHz, C_6D_6) δ 11.7 (s, SiMe), 12.1 (d, J_{C-P} = 6.9 Hz, SiMe), 13.0 (d, J_{C-P} = 1.7 Hz, SiMe), 13.2 (s, SiMe), 85.7 (s, Cp), 128.8 (d, J_{C-P} = 6.7 Hz, PPh$_3$), 129.6 (d, J_{C-P} = 2.2 Hz, PPh$_3$), 134.0 (d, J_{C-P} = 11.2 Hz, PPh$_3$), 139.9 (d, J_{C-P} = 48.4 Hz, PPh$_3$); ^{29}Si NMR (59.6 MHz, C_6D_6) δ 15.9 (d, $^2J_{Si-P}$ = 7.0 Hz), 29.8 (d, $^2J_{Si-P}$ = 19.0 Hz); ^{31}P NMR (122 MHz, C_6D_6) δ 66.5 (s); IR (KBr pellet) 1994 (RuH), 1238 (SiMe), 1092 (SiOSi, asym), 1005 (SiOSi, sym) cm^{-1}; MS (EI, 70 eV) *m/z* 562 (44, M$^+$), 547 (9.4, $M^+ -$ Me), 532 (4.1, $M^+ -$ 2Me), 429 (100, [Cp(Ph$_3$P)Ru]$^+$), 262 (33, (PPh$_3$)$^+$), 133 (19, (SiMe$_2$OSiMe$_2$H)$^+$). Anal. Calcd for $C_{27}H_{33}OPRuSi_2$: C, 57.72; H, 5.93. Found: C, 57.72; H, 6.07.

Another Method for the Preparation of 4. To Cp(Ph$_3$P)$_2$RuMe (129 mg, 183 μmol) placed in a 10 mm o.d. Pyrex tube connected to a vacuum line were added hexane (3.5 mL) and HSiMe$_2$OSiMe$_2$H (107 mg, 799 μmol) by trap-to-trap transfer. The tube was flame-sealed under high vacuum and heated to 90 °C for 84 h. When the tube was cooled to -32 °C, a yellow precipitate was formed. The tube was opened in a glovebox, and removal of the supernatant liquid afforded **4** as a yellow powder (51.6 mg, 92.0 μmol, yield 50%) whose spectroscopic properties were identical with those of **4** as prepared in the preceding experiment.

Cp(Ph$_3$P)Ru(H)$_2$(SiMe$_2$OSiMe$_2$OSiMe$_2$OSiMe$_2$)(H)$_2$Ru(PPh$_3$)Cp (5). Complex **1** (146 mg, 253 μmol) was dissolved in DME (3 mL), and H$_2$O (50 μL, 2.8 mmol) was added at room temperature. Immediately after the addition, volatiles were removed and the yellow oily residue was dissolved in pentane (0.5 mL). Cooling the solution to -95 °C gave a yellow precipitate. On removal of the supernatant liquid and washing of the precipitate with pentane (0.5 mL) followed by drying under vacuum, **5** was obtained as a yellow oil (111 mg, 97.2 μmol, 77% yield). Spectral data for **5**: ^{1}H NMR (300 MHz, C_6D_6) δ -11.73 (4H, d, $^2J_{H-P}$ = 27.2 Hz, RuH), 0.40 (12H, s, SiMe), 0.49 (12H, s, SiMe), 4.82 (10H, s, Cp), 7.01$-$7.70 (30H, m, PPh$_3$); ^{13}C NMR (75.5 MHz, C_6D_6) δ 2.7 (s, SiMe), 16.4 (s, SiMe), 84.7 (s, Cp), 127.8 (d, J_{C-P} = 7.7 Hz, PPh$_3$), 129.3 (s, PPh$_3$), 134.0 (d, J_{C-P} = 8.9 Hz, PPh$_3$), 140.5 (d, J_{C-P} = 35.8 Hz, PPh$_3$); ^{29}Si NMR (59.6 MHz, C_6D_6) δ -25.7 (s, RuSiOSi), 32.3 (d, $^2J_{Si-P}$ = 9.8 Hz, RuSi); ^{31}P NMR (122 MHz, C_6D_6) δ 71.9 (s); IR (hexane solution) 1978 (RuH), 1255 (SiMe), 1238 (SiMe), 1070 (br, SiOSi), 1024 (br, SiOSi) cm^{-1}; MS (DEI) *m/z* 579 (5.0, [Cp(Ph$_3$P)Ru(H)$_2$SiMe$_2$OSiMe$_2$O]$^+$), 563 (3.4, [Cp(Ph$_3$P)Ru(H)$_2$SiMe$_2$OSiMe$_2$]$^+$), 548 (1.8, [Cp(Ph$_3$P)Ru(H)$_2$SiMe$_2$OSiMe]$^+$), 429 (100, [Cp(Ph$_3$P)Ru]$^+$), 262 (35, (PPh$_3$)$^+$). Anal. Calcd for $C_{54}H_{68}O_3P_2Ru_2Si_4$: C, 56.81; H, 6.02. Found: C, 56.51; H, 5.89.

Reaction of 4 with H$_2$O. H$_2$O (8 μL, 0.4 mmol) was added to a DME solution (1 mL) of complex **4** (23.5 mg, 45.0 μmol). On removal of volatiles, **5** was afforded as an orange oil (15.3 mg, 13.4 μmol, yield 60%) whose ^{1}H NMR spectrum was identical with that of **5** formed in the preceding experiment.

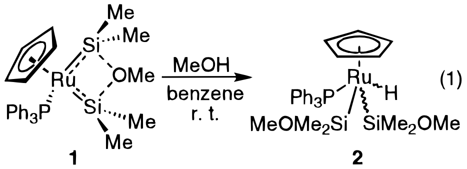


trans isomer *cis* isomer

Figure 1. Possible structures for complex **2**.

Results and Discussion

Addition of 2 equiv of MeOH to a benzene solution of methoxy-bridged bis(silylene) complex **1** resulted in an immediate reaction, and after workup, the hydridobis(silyl)ruthenium complex **2** was obtained as a yellow powder in 83% yield (eq 1). For **2**, two geometric isomers, *trans* and *cis*, are possible (Figure 1). Two silyl groups are equivalent in the *trans* isomer, whereas they are inequivalent in the *cis* isomer. In the ^{29}Si NMR spectrum of **2**, only one doublet was observed at 51.1 ppm ($^2J_{Si-P}$ = 11.6 Hz). Moreover, in the ^{1}H NMR spectrum of **2**, two signals (0.38 and 0.42 ppm) were present in the Si$-$Me region, which can be assigned to mutually diastereotopic Me groups bound to the same silicon atom. These results imply that the main product is the *trans* isomer, and this geometry is different from that of the major isomer (*cis*) of Cp*(Me$_3$P)RuH(SiR$_3$)$_2$ (Cp* = η^5-C$_5$Me$_5$; SiR$_3$ = Si(OEt)$_3$, SiPh$_2$Cl, SiMe$_2$OEt) reported by Tilley et al.[13]

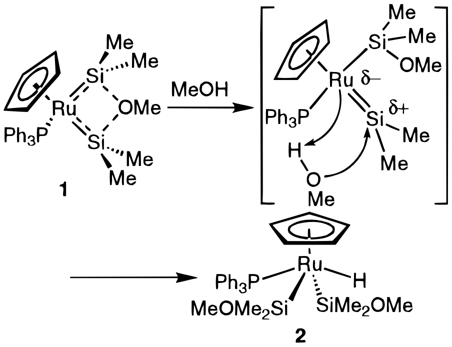


There is another possibility, however, in which **2** is a *cis* isomer and two silyl groups undergo exchange that

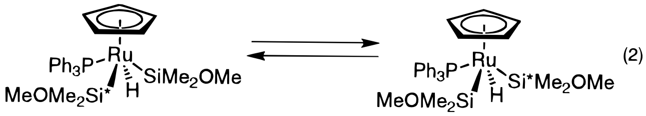
---

[13] Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673.

Scheme 1



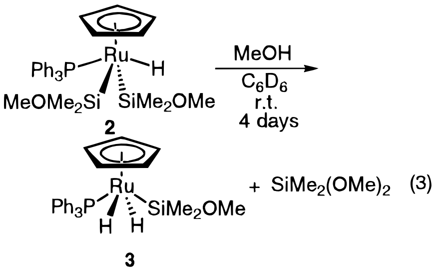
is faster than the NMR time scale (eq 2). This type of fluxionality has been reported by Caulton et al.[14] for $Cp^*Ru(P^iPr_2Ph)(H)_2(SiMe_3)$. This complex has *cis* geometry but shows rapid fluxional behavior in solution to make the two hydride substituents equivalent at 25 °C. However, in the case of **2**, the ^1H NMR spectrum (toluene-d_8) showed neither coalescence nor splitting of signals even when the solution was cooled to −60 °C. Therefore, it is likely that **2** has a structure with the two silyl groups *trans* to each other.



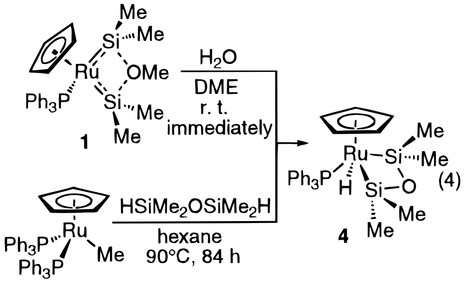
Complex **2** is analogous to *trans*-$Cp'(OC)FeH(SiMe_2OMe)_2$ ($Cp' = \eta^5$-C_5H_5, C_5Me_5), which we obtained by the reaction of the corresponding methoxy-bridged bis(silylene)iron complex with methanol.[5] This complex is the product obtained when MeOH is added to the Si=M double bond and the M−Si bond is retained after the reaction. There are two other reactions of silylene complexes with nucleophiles in which the Si−M bond is retained after the reaction, i.e., that of $[2\text{-}(Me_2NCH_2)C_6H_4]_2Si{=}Cr(CO)_5$ with H_2O[6] and that of $[\{2\text{-}(Me_2NCH_2)C_6H_4\}MeSi{=}FeCp(CO)_2]PF_6$ with MeOH,[7] but in these reactions, the proton originally bound to oxygen is added to the nitrogen atom of a Me_2N group instead of the metal center. In all other known reactions of silylene complexes with nucleophiles, cleavage of silicon−metal bonds occurs.[2b,3,4]

The reaction of **1** with MeOH is considered to be initiated by nucleophilic attack of MeOH at the electrophilic silylene ligand (Scheme 1). It is consistent with the results of MO calculations for silylene complexes, which predict that the Si=M double bond of silylene complexes is polarized in the sense of $Si^{\delta+}$−$M^{\delta-}$.[2b,9,10] The Si−P coupling constant of **2** ($^2J_{Si-P}$ = 11.6 Hz) is significantly smaller than that of **1** ($^2J_{Si-P}$ = 25.0 Hz).[11] This seems to reflect the difference of the Si−Ru−P bond angles between **1** and **2**.

When the reaction mixture of **1** and an excess of MeOH in C_6D_6 was allowed to stand at room temperature, product **2** was observed to react further with MeOH to give the dihydrido silyl complex **3** and $Me_2Si(OMe)_2$ (eq 3). $Me_2Si(OMe)_2$ was characterized by comparing the ^1H, ^{13}C, and ^{29}Si NMR spectra of the reaction mixture with those of a separately prepared authentic sample. The reaction proceeded slowly and was completed in 4 days. In the ^1H NMR spectrum of **3**, the signal for the two hydride ligands appears at −11.80 ppm (d, $^2J_{H-P}$ = 26.8 Hz), and in the IR spectrum, the Ru−H stretching vibration was observed at 1971 cm^{-1}. The variable-temperature ^1H NMR spectra for **3** were also recorded between −60 °C and room temperature. However, even at −60 °C, neither coalescence nor splitting was observed. This clearly shows that **3** has the *trans* structure. Such a structure with two hydride ligands is similar to those of the compounds $[Cp'Ru(P^\frown P)(H)_2]^+$ ($Cp' = C_5H_5$, C_5Me_5; $P^\frown P$ = diphosphines) reported by Simpson et al.,[15] Heinekey et al.,[16] and Morris et al.,[17] $Cp^*(^iPr_3P)Ru(H)_2(SiMePh_2)$ reported by Tilley et al.,[18] $(\eta^6\text{-Ar})Fe(H)_2(SiX_3)_2$ (Ar = benzene, toluene, *p*-xylene; X = Cl, F) reported by Klabunde et al.,[19] and $(\eta^6\text{-Ar}')Ru(H)_2(SiMe_3)_2$ (Ar′ = C_6Me_6, *p*-cymene, benzene) reported by Berry et al.[20] It is considered that, in the secondary reaction, a silyl ligand in **2** undergoes nucleophilic attack by MeOH, resulting in cleavage of the Ru−Si bond. Complex **3** was so sensitive to air and moisture that further purification was not successful.



The reaction of **1** with H_2O was studied. Addition of a small excess (3 equiv) of H_2O to a DME solution of **1** gave the hydrido bis(silyl) complex **4** as a yellow powder in 80% yield (eq 4). When the same reaction was examined in toluene, a hydrophobic solvent, a mixture of complexes **2** and **4** was obtained. This implies that, in the reaction of **1** with H_2O, complex **4** and MeOH are produced. In the reaction in DME, a hydrophilic solvent, only **4** is obtained because H_2O is much more reactive toward **1** than MeOH and **1** reacts with dis-



---

(14) Johnson, T. J.; Coan, P. S.; Caulton, K. G. *Inorg. Chem.* **1993**, *32*, 4594.

(15) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675.

(16) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166.

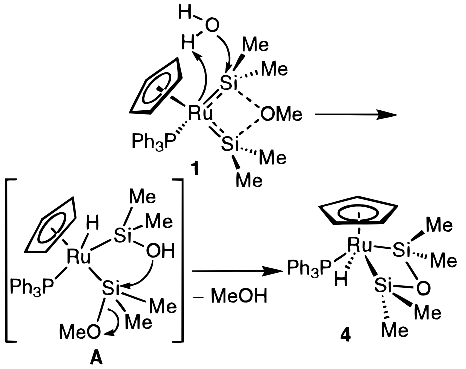
(17) (a) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. (b) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161.

(18) Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5527.

(19) (a) Asirvatham, V. S.; Yao, Z.; Klabunde, K. J. *J. Am. Chem. Soc.* **1994**, *116*, 5493. (b) Yao, Z.; Klabunde, K. J.; Asirvatham, V. S. *Inorg. Chem.* **1995**, *34*, 5289. (c) Yao, Z.; Klabunde, K. J. *Organometallics* **1995**, *14*, 5013.

(20) Djurovich, P. I.; Carroll, P. J.; Berry, D. H. *Organometallics* **1994**, *13*, 2551.

Scheme 2



solved H_2O before it does with MeOH. In toluene, however, H_2O is excluded from the solvent, and H_2O can react with **1** only at the interface between water and the organic phase. This causes the reaction of **1** with MeOH to give **2** to be faster than that with H_2O.

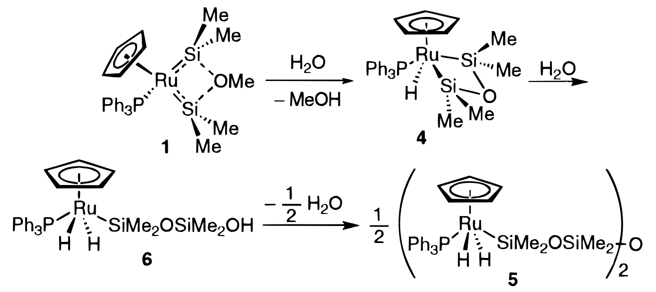
In the ^{1}H NMR spectrum of **4**, the signals of all four methyl groups bound to the two silyl ligands are inequivalent. The ^{29}Si NMR spectrum shows two doublets with very different Si−P coupling constants (7.0 and 19.0 Hz). These observations indicate that **4** is the *cis* isomer. In the IR spectrum of **4**, two sharp bands are observed at 1092 and 1005 cm^{-1}. These are assigned to the asymmetric and symmetric stretching modes of the Si−O−Si bond, respectively. This IR spectral pattern is analogous to those of the metallacycles $L_n\overline{M{-}Si{-}O{-}Si}$ (M = Pt, Pd, Ir, Rh, Fe, Ru) reported by Curtis et al.[21a] These data, as well as the mass spectrum and elemental analysis, indicate that **4** is a metallacycle containing a $\overline{Ru{-}Si{-}O{-}Si}$ chelate ring.

Complex **4** can be obtained also by a different route, namely the thermolysis of $Cp(Ph_3P)_2RuMe$ in the presence of $HSiMe_2OSiMe_2H$ (eq 4). This method is analogous to that employed by Curtis et al. for synthesizing metallacycles $L_n\overline{M{-}Si{-}O{-}Si}$.[21] This result further confirms the structure of **4**.

By analogy with the reaction of complex **1** with MeOH, the initial step of the reaction of **1** with H_2O is considered to be the nucleophilic attack of H_2O at one of the silylene ligands to give intermediate **A** (Scheme 2). In this case, subsequent intramolecular condensation with extrusion of MeOH occurs to afford the metallacycle **4** with an Si−O−Si bond.

Addition of a large excess (11 equiv) of H_2O to a DME solution of **1** gave complex **5** as a yellow oil in 77% yield (Scheme 3). The ^{1}H NMR spectrum of **5** shows only one Ru−H signal at −11.73 ppm ($^2J_{H-P}$ = 27.2 Hz), and it did not show any change even when the sample was cooled to −60 °C. This behavior is similar to that of **3** and is consistent with the *trans* geometry of the $Cp(Ph_3P)Ru(H)_2$ moiety of **5**. In the IR spectrum of **5**, strong broad bands that are characteristic for the Si−O−Si stretching of linear siloxanes[22] appeared at 1070 and 1024 cm^{-1}. In the ^{29}Si NMR spectrum, a singlet (−25.7 ppm) and a doublet (32.3 ppm, $^2J_{Si-P}$ = 9.8 Hz) were observed. The singlet is in the region typical of the $SiMe_2$ moiety of polysiloxanes,[23] and the doublet signals can be assigned to the silicon atoms directly bonded to $Cp(Ph_3P)Ru(H)_2$. From these data we deduce that **5** is a dinuclear complex bridged by a tetrasiloxane. In the mass spectrum, the molecular ion was not observed, but the molecular weight measurement, using a vapor pressure osmometer with benzene as solvent and benzil as a molecular weight standard, gave a value (1190) which is close to the calculated one (1142) for the tetrasiloxane structure of **5**.

Scheme 3



The complex **5** was obtained also by the reaction of **4** with H_2O in DME. A possible formation mechanism for **5** is given in Scheme 3. The complex **1** reacts with 1 equiv of H_2O to give **4**. In a manner similar to the reaction of bis(methoxysilyl) complex **2** with MeOH, a silyl ligand of **4** is attacked by another H_2O molecule and the ring is opened at the Ru−Si bond to form $Cp(Ph_3P)Ru(H)_2SiMe_2OSiMe_2OH$ (**6**). Subsequent dehydration from two molecules of **6** afforded the condensation product **5**.

These experimental results indicate that nucleophilic addition of MeOH or H_2O at the Si═Ru double bond in **1** is faster than the nucleophilic cleavage of the Si−Ru single bonds in **2** or **4**. This may be due in part to the σ* orbital of the MeO→Si dative bond in **1**, which obviously is lower in energy than those of the normal covalent Si−O or Si−C bonds in **2** or **4**, and thus the former orbital interacts with the HOMO of nucleophiles more strongly.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics (No. 07216206) from the Ministry of Education, Science and Culture of Japan and a Kurata Research Grant from the Kurata Foundation. We thank Shin-Etsu Chemical Co., Ltd., and Toray Dow Corning Silicone Co., Ltd., for their gifts of silicon compounds.

Supporting Information Available: A figure giving the ^{1}H NMR spectrum of **3** (1 page). Ordering information is given on any current masthead page.

OM961031Z

---

[21] (a) Curtis, M. D.; Greene, J. *J. Am. Chem. Soc.* **1978**, *100*, 6362. (b) Curtis, M. D.; Greene, J.; Butler, W. M. *J. Organomet. Chem.* **1979**, *164*, 371. (c) Greene, J.; Curtis, M. D. *Inorg. Chem.* **1978**, *17*, 2324. (d) Bell, L. G.; Gustavson, W. A.; Thanedar, S., Curtis, M. D. *Organometallics* **1983**, *2*, 740.

[22] Crompton, T. R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 6, p 393.

[23] Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 8, p 511.