

Electronic Supplementary Information

Reactions of a Hydrido(hydrosilylene)ruthenium Complex with Carbonyl Compounds

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1. Experimental Details

General Procedures. All manipulations were performed using either standard Schlenk techniques under nitrogen or argon atmosphere, or vacuum line techniques, or in a glovebox under nitrogen atmosphere. $\text{Cp}^*(\text{CO})(\text{H})\text{Ru}=\text{Si}(\text{H})\{\text{C}(\text{SiMe}_3)_3\}$ (**2**)¹ was prepared by the literature procedure. Toluene, hexane, benzene-*d*₆, and toluene-*d*₈ were dried over calcium hydride and then with a potassium mirror, and transferred into a reaction vessel under vacuum. Pentane, hexamethyldisiloxane, and dichloromethane-*d*₂ were dried over calcium hydride and with molecular sieves. Acetone, acetophenone, benzaldehyde, and propionaldehyde were distilled under a nitrogen atmosphere or under a reduced pressure. Benzophenone was used as it was purchased. ¹H, ¹³C{¹H}, and ²⁹Si{¹H} NMR spectra were recorded on a Bruker AVANCE-300 Fourier transform spectrometer. IR spectra were obtained on a HORIBA FT-730 spectrometer at room temperature. Elemental analysis and mass spectrometry were performed at Research and Analytical Center for Giant Molecules, Tohoku University.

1.1 Reaction of $\text{Cp}^*(\text{CO})(\text{H})\text{Ru}=\text{Si}(\text{H})\{\text{C}(\text{SiMe}_3)_3\}$ (**2**) with acetone.

(a) NMR experiment: In an NMR tube equipped with a rubber septum on the top, a benzene-*d*₆ solution of **2** (13 mg, 0.025 mmol) containing hexamethylbenzene (ca. 2 mg) as an internal standard was prepared. After measuring a ¹H NMR spectrum of the solution, acetone (2.2 μL, 0.030 mmol) was added to it by a microsyringe at room temperature. The ¹H NMR spectrum of the reaction mixture showed the formation of $\text{Cp}^*(\text{CO})(\text{H})_2\text{Ru}[\text{Si}(\text{H})\{\text{OC}(=\text{CH}_2)\text{Me}\}\text{C}(\text{SiMe}_3)_3]$ (**3a**) in 100% NMR yield.

(b) Isolation of $\text{Cp}^*(\text{CO})(\text{H})_2\text{Ru}[\text{Si}(\text{H})\{\text{OC}(=\text{CH}_2)\text{Me}\}\text{C}(\text{SiMe}_3)_3]$ (3a**):** To a Pyrex glass tube (2 cm φ, 17 cm) equipped with a Teflon needle valve on the top containing **2** (87 mg, 0.17 mmol) was added hexane (5 mL) by a trap-to-trap transfer technique on a vacuum line. After addition of acetone (18 μL, 0.24 mmol) at room temperature, the mixture was stirred for 5 min. Volatiles were removed under vacuum. The residue was recrystallised from hexane (1 mL) at -30 °C to afford **3a** as yellow crystals in 71% yield (68 mg, 0.12 mmol). ¹H NMR (300 MHz, CD₂Cl₂): δ = -9.80 (d, ³J_{HH} = 4.8 Hz, ²J_{SiH} = 23.8 Hz, 2H, RuH₂), 0.23 (s, 27H, SiMe), 1.76 (s, 3H, OCCH₃), 1.93 (s, 15H, Cp*), 4.00 (s, 1H, OC=CH), 4.29 (s, 1H, OC=CH), 5.96 (t, ³J_{HH} = 4.8 Hz, ¹J_{SiH} = 207.1 Hz, 1H, SiH). ¹³C{¹H} NMR (75.5 MHz, CD₂Cl₂, 240 K): δ = 4.3 (SiMe), 5.2 (C(SiMe₃)₃), 10.3 (C₅Me₅), 22.8 (OCCH₃), 92.8 (C=CH₂), 99.1 (C₅Me₅), 155.8 (SiOC), 206.8 (CO). ²⁹Si{¹H} NMR (59.6 MHz, C₆D₆): δ = -1.2 (SiMe), 20.4 (SiH). IR (KBr pellet): 1967 (vs, ν_{CO}) cm⁻¹. MS (EI, 70 eV) 584 (*M*⁺, 43), 569 (*M*⁺-CH₃, 11), 538 (*M*⁺-3CH₃-H, 11), 73 (SiMe₃, 41). Anal. Calcd. for C₂₄H₅₀O₂Si₄Ru: C, 49.35; H, 8.63. Found: C, 49.43; H, 8.55%.

1.2 Reaction of $\text{Cp}^*(\text{CO})(\text{H})\text{Ru}=\text{Si}(\text{H})\{\text{C}(\text{SiMe}_3)_3\}$ (**2**) with acetophenone.

(a) NMR experiment: In a procedure similar to 1.1 (a), a benzene-*d*₆ solution of **2** (9.0 mg, 0.017 mmol) containing hexamethylbenzene was treated with acetophenone (2.0 μL, 0.017 mmol) to afford $\text{Cp}^*(\text{CO})(\text{H})_2\text{Ru}[\text{Si}(\text{H})\{\text{OC}(=\text{CH}_2)\text{Ph}\}\text{C}(\text{SiMe}_3)_3]$ (**3b**) in 100% NMR yield.

(b) Isolation of $\text{Cp}^*(\text{CO})(\text{H})_2\text{Ru}[\text{Si}(\text{H})\{\text{OC}(=\text{CH}_2)\text{Ph}\}\text{C}(\text{SiMe}_3)_3]$ (3b**):** In a procedure similar to

1.1 (b), to a hexane solution (5 mL) of **2** (82 mg, 0.16 mmol) was added acetophenone (18 μ L, 0.15 mmol) at room temperature and the mixture was stirred for 3 min. After removal of volatiles, recrystallisation of the residue from pentane (1 mL) at -30 °C afforded **3b** as yellow crystals in 81% yield (82 mg, 0.13 mmol). ^1H NMR (300 MHz, CD_2Cl_2): $\delta = -9.71$ (d, $^3J_{\text{HH}} = 4.8$ Hz, $^2J_{\text{SiH}} = 23.8$ Hz, 2H, RuH₂), 0.28 (s, 27H, SiMe), 1.87 (s, 15H, Cp*), 4.46 (d, $^2J_{\text{HH}} = 0.9$ Hz, 1H, OC=CH), 5.12 (d, $^2J_{\text{HH}} = 0.9$ Hz, 1H, OC=CH), 6.09 (t, $^3J_{\text{HH}} = 4.8$ Hz, $^1J_{\text{SiH}} = 207.1$ Hz, 1H, SiH), 7.22-7.35 (m, 3H, Ph), 7.62-7.70 (m, 2H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2 , 243 K): $\delta = 4.4$ (SiMe), 5.4 (C(SiMe₃)₃), 10.3 (C₅Me₅), 93.1 (C=CH₂), 99.3 (C₅Me₅), 125.6 (Ph), 127.76 (Ph), 127.80 (Ph), 138.0 (Ph), 155.0 (SiOC), 206.9 (CO). $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.6 MHz, CD_2Cl_2 , 243 K): $\delta = -1.3$ (SiMe), 25.9 (SiH). IR (KBr pellet) 1955 (vs, ν_{CO}) cm^{-1} . Anal. Calcd. for C₂₉H₅₂O₂Si₄Ru: C, 53.91; H, 8.11. Found: C, 53.71; H, 8.34%.

1.3 Reaction of Cp*(CO)(H)Ru=Si(H){C(SiMe₃)₃} (**2**) with benzophenone.

(a) NMR experiment: In a procedure similar to 1.1 (a), to a benzene-*d*₆ solution of **2** (11 mg, 0.021 mmol) was added benzophenone (4 mg, 0.022 mmol) at room temperature. After 2 h, Cp*(CO)(H)Ru=Si(OCHPh₂){C(SiMe₃)₃} (**4**) was formed in 76% NMR yield. The rather low yield of **4** is due to its thermal instability at room temperature.

(b) Isolation of Cp*(CO)(H)Ru=Si(OCHPh₂){C(SiMe₃)₃} (4**)** In a procedure similar to 1.1 (b), **2** (107 mg, 0.203 mmol) and benzophenone (37 mg, 0.20 mmol) in hexane (5 mL) were stirred for 2 h at room temperature. After removal of volatiles, recrystallisation of the residue from hexamethyldisiloxane (1 mL) at -30 °C gave **4** as yellow crystals in 64% yield (89 mg, 0.13 mmol). Analytically pure samples were obtained by recrystallisation from toluene/hexane (1 : 1) mixture at -30 °C. ^1H NMR (300 MHz, CD_2Cl_2): $\delta = -11.65$ (s, $^2J_{\text{SiH}} = 20.5$ Hz, 1H, RuH), 0.28 (s, 27H, SiMe), 1.97 (s, 15H, Cp*), 7.07 (s, 1H, OCH), 7.16-7.39 (m, 6H, Ph), 7.42-7.61 (m, 4H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2): $\delta = 6.6$ (SiMe), 11.9 (C₅Me₅), 35.9 (C(SiMe₃)₃), 81.5 (OCH), 96.7 (C₅Me₅), 127.4 (Ph), 127.7 (Ph), 127.9 (Ph), 128.5 (Ph), 129.0 (Ph), 143.7 (Ph), 144.1 (Ph), 207.8 (CO). $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.6 MHz, CD_2Cl_2): $\delta = -2.5$ (SiMe), 266.1 (SiH). IR (C₆D₆): 1965 (w, ν_{SiH}), 1915 (vs, ν_{CO}) cm^{-1} . Anal. Calcd. for C₃₄H₅₄O₂Si₄Ru: C, 57.66; H, 7.69. Found: C, 57.58, H, 7.66%.

1.4 Reaction of Cp*(CO)(H)Ru=Si(H){C(SiMe₃)₃} (**2**) with benzaldehyde

(a) NMR experiment: In a procedure similar to 1.1 (a), **2** (11 mg, 0.021 mmol) was treated with benzaldehyde (2.1 μ L, 0.021 mmol) in benzene-*d*₆ and were stirred for 4 h at room temperature to produce Cp*(CO)Ru{CHPhOSiH₂C(SiMe₃)₃} (**5a**) in 55% NMR yield.

(b) Isolation of Cp*(CO)Ru{CHPhOSiH₂C(SiMe₃)₃} (5a**):** In a procedure similar to 1.1 (b), **2** (141 mg, 0.268 mmol) and benzaldehyde (27 μ L, 0.27 mmol) in hexane (5 mL) was stirred for 4 h at room temperature. After removal of volatiles, recrystallisation of the residue from toluene/hexane (1 : 2) mixture at -30 °C afforded **5a** as yellow crystals in 56% yield (93 mg, 0.15 mmol). ^1H NMR (300 MHz, C₆D₆): $\delta = -11.59$ (d, $^2J_{\text{HH}} = 12.8$ Hz, $^1J_{\text{SiH}} = 82.7$ Hz, 1H, η^2 -SiH), 0.45 (s, 27H, SiMe), 1.48 (s, 15H, Cp*), 5.65 (s, 1H, RuCH), 6.44 (d, $^2J_{\text{HH}} = 12.8$ Hz, $^1J_{\text{SiH}} = 226.5$ Hz, 1H, SiH), 6.96-7.07 (m, 1H, Ph), 7.29-7.34 (m, 2H, Ph), 7.50-7.56 (m, 2H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2): $\delta = 4.1$ (SiMe), 10.0 (C₅Me₅), 65.3 (RuCH), 97.5 (C₅Me₅), 123.6 (Ph), 123.9 (Ph), 127.5 (Ph), 155.3 (Ph), 209.2 (CO). The signal of C(SiMe₃)₃ could not be assigned. Complex **5a** exists as an isomeric mixture in solution. The SiMe and C₅Me₅ of isomer signals appeared the same region. $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.6 MHz, toluene-*d*₈): $\delta = -16.3$ (SiH), -1.0 (SiMe). IR (C₆D₆): 2094 (w, ν_{SiH}), 1952 (vs, ν_{CO}) cm^{-1} . Exact Mass (ESI, positive): Calcd. for [C₂₈H₅₀O₂Si₄Ru + Na]⁺: 655.1824. Found: 655.1823. Anal. Calcd. for C₂₈H₅₀O₂Si₄Ru: C, 53.20; H, 7.97. Found: C, 53.34; H, 7.92%.

1.5 Reaction of Cp*(CO)(H)Ru=Si(H){C(SiMe₃)₃} (**2**) with propionaldehyde.

(a) NMR tube experiment: In a procedure similar to 1.1 (a), a benzene-*d*₆ solution of **2** (9 mg, 0.017

mmol) was treated with propionaldehyde (1.2 μL , 0.017 mmol) at room temperature to form instantaneously $\text{Cp}^*(\text{CO})\text{Ru}\{\text{CH}_2\text{OSiH}_2\text{C}(\text{SiMe}_3)_3\}$ (**5b**) in 78% NMR yield.

(b) Isolation of $\text{Cp}^*(\text{CO})\text{Ru}\{\text{CH}_2\text{OSiH}_2\text{C}(\text{SiMe}_3)_3\}$ (5b**):** In a procedure similar to 1.1 (b), to **2** (96 mg, 0.18 mmol) in hexane (5 mL) was added propionaldehyde (16 μL , 0.22 mmol) at room temperature and the mixture was stirred for 10 min. After removal of volatiles, recrystallisation of the residue from toluene/hexamethyldisiloxane (1 : 2) at -30°C afforded **5b** as yellow crystals in 61% yield (65 mg, 0.11 mmol). ^1H NMR (300 MHz, C_6D_6): $\delta = -11.46$ (d, $^2J_{\text{HH}} = 11.7$ Hz, $^1J_{\text{SiH}} = 75.0$ Hz, 1H, η^2 -SiH), 0.44 (s, 27H, SiMe), 1.26 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H, $\text{RuCHCH}_2\text{CH}_3$), 1.50 (s, 15H, Cp*), 1.87-2.02 (m, 1H, $\text{RuCHCH}_2\text{CH}_3$), 2.58-2.77 (m, 1H, $\text{RuCHCH}_2\text{CH}_3$), 4.10 (dd, $^3J_{\text{HH}} = 2.6$ Hz, $^4J_{\text{HH}} = 10.6$ Hz, 1H, $\text{RuCHCH}_2\text{CH}_3$), 6.19 (d, $^2J_{\text{HH}} = 11.7$ Hz, $^1J_{\text{SiH}} = 224.7$ Hz, 1H, SiH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta = 4.4$ (SiMe), 6.2 ($\text{C}(\text{SiMe}_3)_3$), 9.5 (C_5Me_5), 14.4 ($\text{RuCHCH}_2\text{CH}_3$), 40.9 ($\text{RuCHCH}_2\text{CH}_3$), 65.9 ($\text{RuCHCH}_2\text{CH}_3$), 97.5 (C_5Me_5), 209.7 (CO). $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.6 MHz, C_6D_6): $\delta = -18.5$ (SiH), -1.1 (SiMe). IR (C_6D_6): 2083 (w, ν_{SiH}), 1940 (vs, ν_{CO}) cm^{-1} . Anal. Calcd. for $\text{C}_{24}\text{H}_{50}\text{O}_2\text{Si}_4\text{Ru}$: C, 49.35; H, 8.63. Found: C, 49.06; H, 8.74%.

1.6 Thermal conversion of **5a** to $\text{Cp}^*(\text{CO})(\text{H})\text{Ru}=\text{Si}(\text{OCH}_2\text{Ph})\{\text{C}(\text{SiMe}_3)_3\}$ (**6a**)

(a) NMR experiment: A degassed C_6D_6 solution of **5a** (8 mg, 0.01 mmol) containing hexamethylbenzene (ca. 2 mg) as an internal standard in an NMR sealed tube was heated at 50°C for 40 h. The ^1H NMR spectrum of the reaction mixture showed the signals for $\text{Cp}^*(\text{CO})(\text{H})\text{Ru}=\text{Si}(\text{OCH}_2\text{Ph})\{\text{C}(\text{SiMe}_3)_3\}$ (**6a**) in 76% NMR yield.

(b) Isolation of $\text{Cp}^*(\text{CO})(\text{H})\text{Ru}=\text{Si}(\text{OCH}_2\text{Ph})\{\text{C}(\text{SiMe}_3)_3\}$ (6a**):** A degassed toluene solution of **5a** (98 mg, 0.16 mmol) in a sealed Pyrex glass tube was heated at 50°C for 40 h. Volatiles were removed under vacuum. The residue was recrystallised from hexamethyldisiloxane (1 mL) at -30°C to afford **6a** as yellow crystals in 48% yield (48 mg, 0.076 mmol). ^1H NMR (300 MHz, cyclohexane- d_{12}): $\delta = -11.66$ (s, $^2J_{\text{SiH}} = 18.7$ Hz, 1H, RuH), 0.27 (s, 27H, SiMe), 2.04 (s, 15H, Cp*), 5.15 (d, $^2J_{\text{HH}} = 11.4$ Hz, 1H, OCH_2), 5.18 (d, $^2J_{\text{HH}} = 11.4$ Hz, 1H, OCH_2), 7.13-7.28 (m, 3H, Ph), 7.38-7.45 (m, 2H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, cyclohexane- d_{12}): $\delta = 6.3$ (SiMe), 12.1 (C_5Me_5), 36.5 ($\text{C}(\text{SiMe}_3)_3$), 69.4 (OCH_2), 96.4 (C_5Me_5), 128.3 (Ph), 128.7 (Ph), 130.2 (Ph), 139.7 (Ph), 206.8 (CO). $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.6 MHz, cyclohexane- d_{12}): $\delta = 3.1$ (SiMe), 274.2 (RuSi). IR (cyclohexane- d_{12}): 1975 (vs, ν_{CO}) cm^{-1} . Anal. Calcd. for $\text{C}_{28}\text{H}_{50}\text{O}_2\text{Si}_4\text{Ru}$: C, 53.20; H, 7.97. Found: C, 53.09; H, 7.70%.

1.7 Thermal conversion of **5b** to $\text{Cp}^*(\text{CO})(\text{H})\text{Ru}=\text{Si}(\text{OCH}_2\text{Et})\{\text{C}(\text{SiMe}_3)_3\}$ (**6b**)

(a) NMR experiment: In a procedure similar to 1.6 (a), a C_6D_6 solution of **5b** (8 mg, 0.01 mmol) was heated at 40°C for 43 h to afford $\text{Cp}^*(\text{CO})(\text{H})\text{Ru}=\text{Si}(\text{OCH}_2\text{Et})\{\text{C}(\text{SiMe}_3)_3\}$ (**6b**) in 94% NMR yield.

(b) Isolation of $\text{Cp}^*(\text{CO})(\text{H})\text{Ru}=\text{Si}(\text{OCH}_2\text{Et})\{\text{C}(\text{SiMe}_3)_3\}$ (6b**):** In a procedure similar to 1.6 (b), **5b** (65 mg, 0.11 mmol) in hexane was heated at 40°C for 43 h. After removal of volatiles, recrystallisation of the residue from hexamethyldisiloxane (0.5 mL) at -30°C afforded **6b** as yellow crystals in 65% yield (42 mg, 0.072 mmol). ^1H NMR (300 MHz, C_6D_6): $\delta = -11.43$ (s, $^2J_{\text{SiH}} = 19.0$ Hz, 1H, RuH), 0.46 (s, 27H, SiMe), 0.87 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.66-1.81 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.92 (s, 15H, Cp*), 4.03-4.20 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta = 6.2$ (SiMe), 10.6 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 11.8 (C_5Me_5), 25.7 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 35.7 ($\text{C}(\text{SiMe}_3)_3$), 68.3 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 96.0 (C_5Me_5), 207.5 (CO). $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.6 MHz, C_6D_6): $\delta = -2.8$ (SiMe), 266.7 (RuSi). IR (C_6D_6): 1909 (vs, ν_{CO}) cm^{-1} . Anal. Calcd. for $\text{C}_{24}\text{H}_{50}\text{O}_2\text{Si}_4\text{Ru}$: C, 49.35; H, 8.63. Found: C, 48.97; H, 8.37%.

2. X-ray analysis of **4**

Diffraction measurements were made on a RIGAKU RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-K α radiation. A crystal of **4** was coated with

liquid paraffin and were mounted on a nylon loop. The structure was solved by Patterson and Fourier transform methods. All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters based on F^2 with all reflections. All calculations were performed using SHELXS-97.² A total of 44 images, corresponding to 220.0° oscillation angles, were collected with 2 different goniometer settings. Exposure time was 48 sec/deg for **4**. Readout was performed in the 0.100 mm pixel mode. Empirical absorption collections were made using the program NUMABS. The positions of the hydrogen atoms of the Si–H and Ru–H groups were not found from the Fourier-difference electron-density. All other hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. The final residue $R1$ and the weighted $wR2$ were $R1 = 0.132$ and $wR2 = 0.315$ for 12097 reflections with $I > 2\sigma(I)$ and $R1 = 0.148$, $wR2 = 0.326$ for all data. We tried repeated recrystallisation by changing the solvent and conditions to get better crystals, but all our efforts resulted in failure.

Table S1. Crystal Data and Structure Refinement for $\text{Cp}^*(\text{CO})(\text{H})\text{Ru}=\text{Si}(\text{OCHPh}_2)\{\text{C}(\text{SiMe}_3)_3\}$ (**4**)

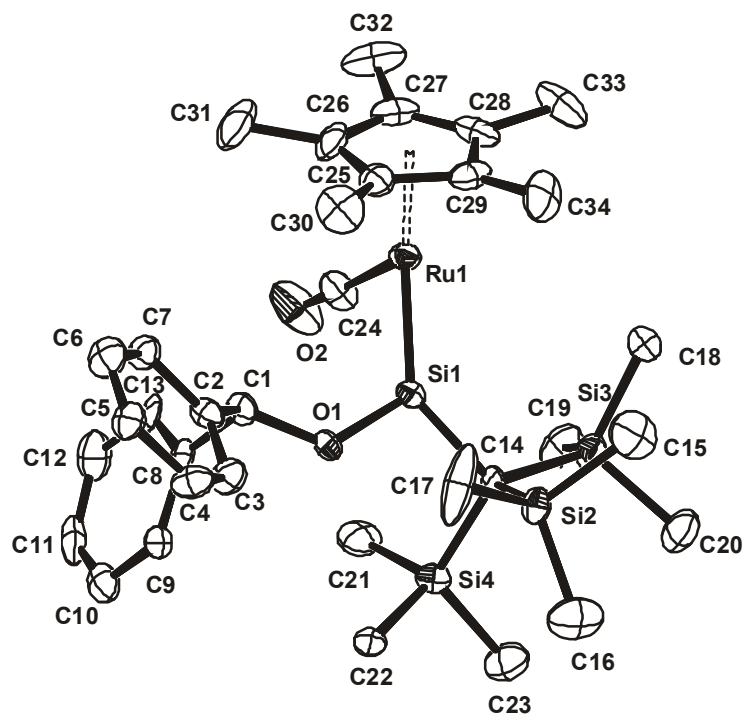
Empirical formula	$\text{C}_{34}\text{H}_{54}\text{O}_2\text{Si}_4\text{Ru}$
Formula weight	708.20
Temperature	150 K
Wavelength	0.71069 Å
Crystal system	triclinic
Space group	$P-1$
Unit cell dimensions	$a = 9.6657(4)$ Å $b = 19.8503(16)$ Å $c = 20.2818(17)$ Å $\alpha = 75.303(5)^\circ$ $\beta = 79.313(5)^\circ$ $\gamma = 87.413(3)^\circ$
Volume	$3698.8(5)$ Å ³
Z	4
Density (calculated)	1.272 g/cm ³
Absorption coefficient	0.581 mm ⁻¹
$F(000)$	1496
Crystal size	$0.37 \times 0.37 \times 0.32$ mm ³
Theta range for data collection	1.06 to 27.48° .
Index ranges	$-12 \leq h \leq 11$, $-25 \leq k \leq 25$, $-26 \leq l \leq 26$
Reflections collected	27413
Independent reflections	14088 [$R(\text{int}) = 0.070$]
Reflections with $I > 2\sigma(I)$	12097
Completeness to theta = 27.48°	83.0 %
Max. and min. transmission	0.8360 and 0.8138
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14088 / 0 / 767
Goodness-of-fit on F^2	1.190
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.132$, $wR2 = 0.315$
R indices (all data)	$R1 = 0.148$, $wR2 = 0.326$
Largest diff. peak and hole	6.823 and -2.224 e.Å ⁻³

$$^a R1 = \frac{\sum ||Fo| - |Fc||}{\sum |Fo|}$$

$$wR2 = \left[\frac{\sum [w(Fo^2 - Fc^2)^2]}{\sum [w(Fo^2)^2]} \right]^{0.5}$$

$$\text{calc } w = 1 / [\sigma^2(F_o^2) + (0.0834P)^2 + 99.7863P] \text{ where } P = (F_o^2 + 2F_c^2) / 3.$$

Molecule A



Molecule B

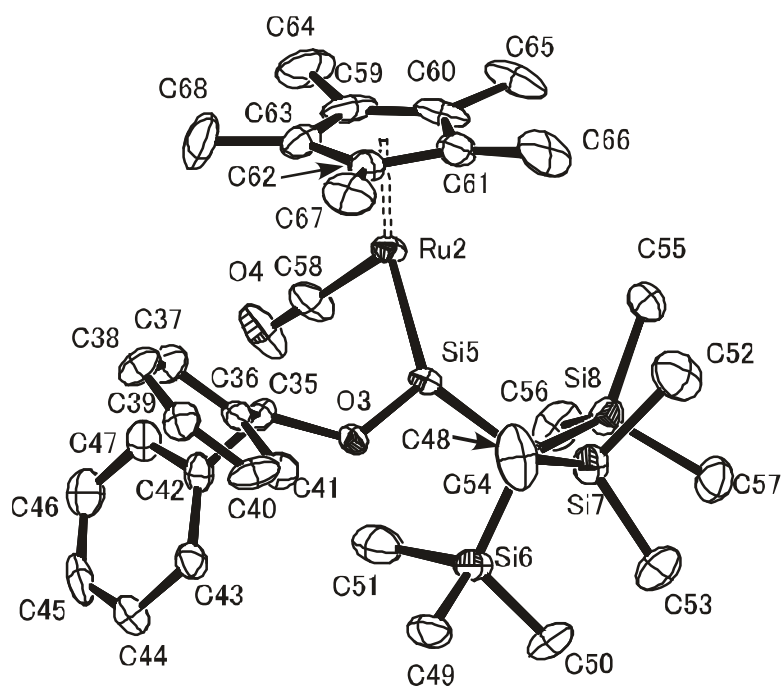


Figure S1. ORTEP drawing of **4** with 50% thermal probability ellipsoids.

Table S2. Selected bond lengths [Å] and angles [°] for **4**

Molecule A		Ru(2)-C(58)	1.840(14)
Ru(1)-C(24)	1.834(12)	Ru(2)-Si(5)	2.241(3)
Ru(1)-Si(1)	2.236(3)	Ru(2)-C(60)	2.249(12)
Ru(1)-C(27)	2.252(12)	Ru(2)-C(59)	2.261(12)
Ru(1)-C(28)	2.256(12)	Ru(2)-C(61)	2.266(14)
Ru(1)-C(29)	2.268(12)	Ru(2)-C(62)	2.278(12)
Ru(1)-C(26)	2.275(13)	Ru(2)-C(63)	2.301(12)
Ru(1)-C(25)	2.284(12)	Si(5)-O(3)	1.664(7)
Si(1)-O(1)	1.650(8)	Si(5)-C(48)	1.892(11)
Si(1)-C(14)	1.864(12)	O(3)-C(35)	1.440(12)
O(1)-C(1)	1.447(14)	O(4)-C(58)	1.168(17)
O(2)-C(24)	1.150(15)		
Molecule B			
Molecule A		Molecule B	
C(24)-Ru(1)-Si(1)	89.0(4)	C(58)-Ru(2)-Si(5)	89.3(4)
C(24)-Ru(1)-C(27)	101.2(5)	Si(5)-Ru(2)-C(59)	165.1(4)
O(1)-Si(1)-C(14)	101.6(4)	O(3)-Si(5)-C(48)	103.1(4)
O(1)-Si(1)-Ru(1)	123.2(3)	O(3)-Si(5)-Ru(2)	121.8(3)
C(14)-Si(1)-Ru(1)	135.0(3)	C(48)-Si(5)-Ru(2)	134.9(3)
C(1)-O(1)-Si(1)	123.6(6)	C(35)-O(3)-Si(5)	123.4(7)
O(1)-C(1)-C(2)	111.3(9)	O(3)-C(35)-C(42)	110.1(9)
O(1)-C(1)-C(8)	109.3(9)	O(3)-C(35)-C(36)	112.4(9)
C(2)-C(1)-C(8)	111.2(9)	C(42)-C(35)-C(36)	109.7(9)

References:

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- 2 G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1997.