

Synthesis and Structure of a Hydrido(hydrosilylene)ruthenium Complex and Its Reactions with Nitriles**

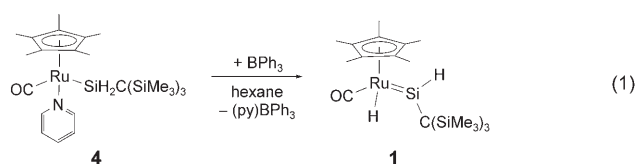
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Transition-metal–silylene complexes have attracted much attention during the last two decades, as they are considered key intermediates in various transformation reactions of organosilicon compounds.^[1] Numerous silylene complexes have been prepared and their reactivities investigated, but clear-cut reactions of silylene complexes with substrates have been limited, because two bulky groups on the silylene ligand, which have been necessary to stabilize the silylene complexes, only allowed access of very small substrate molecules to the reactive silylene silicon site. Recently, Tilley et al.^[2] and our group^[3] have succeeded in synthesizing the silylene complexes having a hydrogen atom on the silylene ligand, and demonstrated that these complexes can react cleanly even with normal-sized substrate molecules such as ketones, oxiranes, and nitriles. These results imply that silylene complexes having a less sterically hindered and more reactive Si–H bond on the silylene ligand could develop into a new rich field in the chemistry of silylene complexes. Herein we report the synthesis of the first neutral hydrido(hydrosilylene)ruthenium complex $[\text{Cp}^*(\text{CO})(\text{H})\text{Ru}=\text{Si}(\text{H})\{\text{C}(\text{SiMe}_3)_3\}]$ (**1**, $\text{Cp}^* = \text{C}_5\text{Me}_5$) utilizing a new synthetic approach, the full structural characterization of **1**, and C–C bond activation of nitriles by this complex through intermediate formation of an agostic complex with $\eta^2\text{-Si-H}$ coordination.

We reported the synthesis of a tungsten hydrido(hydrosilylene) complex $[\text{Cp}^*(\text{CO})_2(\text{H})\text{W}=\text{Si}(\text{H})\{\text{C}(\text{SiMe}_3)_3\}]$ (**2**) by a photoreaction.^[3a] Thus, a similar method was applied for the synthesis of the ruthenium analogue **1**: a C_6D_6 solution of $[\text{Cp}^*\text{Ru}(\text{CO})_2\text{Me}]$ and $\text{H}_3\text{SiC}(\text{SiMe}_3)_3$ was irradiated with UV light at about 5 °C. However, instead of **1**, silyl complex $[\text{Cp}^*(\text{CO})_2\text{Ru}\{\text{SiH}_2\text{C}(\text{SiMe}_3)_3\}]$ (**3**) formed in 76 % yield as determined by NMR spectroscopy. Conversion of **3** into **1** by removal of CO was unsuccessful even on repeated irradiation–degassing cycles.

Synthesis of **1** was finally achieved by the action of BPh_3 on $[\text{Cp}^*(\text{CO})(\text{py})\text{Ru}\{\text{SiH}_2\text{C}(\text{SiMe}_3)_3\}]$ [**4**, $\text{py} = \text{pyridine}$, Eq. (1)], which was prepared by the reaction of $[\text{Cp}^*\text{Ru}-$

$(\text{CO})(\text{py})\text{Me}]^{[4]}$ with $\text{H}_3\text{SiC}(\text{SiMe}_3)_3$. Abstraction of pyridine with BPh_3 occurred immediately, and complex **1** was obtained in 71 % yield as orange crystals. The ^1H NMR spectrum of **1** has a signal for the SiH hydrogen at $\delta = 9.14$ ppm, which is in a typical chemical shift range for the hydrogen atom on an sp^2 silicon atom ($\delta = 6.7\text{--}12.1$ ppm).^[2b,c,3a,5] A resonance arising from the RuH hydrogen appears at $\delta = -11.19$ ppm with no satellite signals, in contrast to that of WH for **2**, which has satellite signals with $^2J_{\text{SiH}} = 28.6$ Hz.^[3a] This indicates that, unlike **2**, complex **1** does not have strong interligand interaction between the silylene and hydrido ligands.^[6]



The molecular structure of **1** was determined by X-ray crystallography (Figure 1).^[7] The Ru1–Si1 bond (2.220(2) Å) is the shortest of the base-free silylene ruthenium complexes

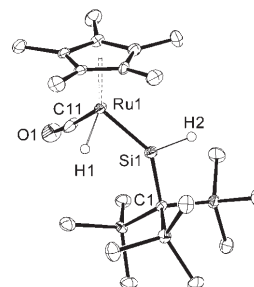


Figure 1. ORTEP drawing of **1** (thermal ellipsoids set at 50% probability). Hydrogen atoms attached to carbon atoms omitted for clarity.

(2.2264–2.33 Å).^[8] The sum of the bond angles around the silylene silicon atom is 359(2)°, which is consistent with sp^2 hybridization. The Si1–H1 bond length is 2.41 Å, which is much longer than those for **2** (1.71(6) Å) and a normal Si–H bond (< 2.0 Å).^[6] Clearly, there is no bonding interaction between them, which is consistent with the above-mentioned NMR spectroscopy result.

DFT calculations were carried out to clarify the origin of the difference in bonding between **1** and **2**.^[9] In a model complex of **2**, $[\text{Cp}(\text{CO})_2(\text{H})\text{W}=\text{Si}(\text{H})\{\text{C}(\text{SiH}_3)_3\}]$ (**2'**, $\text{Cp} = \text{C}_5\text{H}_5$), the direction and symmetry of the W–H bonding orbital is suitable for overlapping with the vacant p orbital of

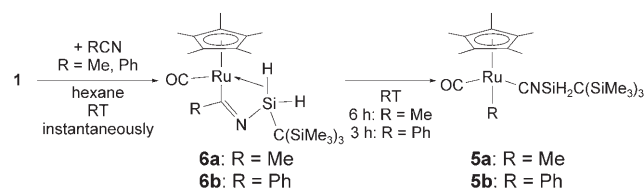
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the silylene ligand. In contrast, in a model complex of **1**, [Cp(CO)(H)Ru=Si(H){C(SiH₃)₃}] (**1'**), the Ru–H bonding orbital is directed away from the silylene p orbital, and cannot interact efficiently with it. This difference apparently arises from the different geometry around the metal center: **1'** adopts a three-legged piano-stool geometry, while **2'** has a four-legged piano-stool geometry. The details of this theoretical study will be reported elsewhere.

The reactivity of **1** toward nitriles was examined. We reported that the reaction of tungsten complex **2** with nitriles gave stoichiometric hydrosilylation products.^[3b] In contrast, the reaction of ruthenium complex **1** with nitriles proceeded slowly at room temperature with C–C bond cleavage of nitriles to afford silylisocyanide complexes [Cp*(CO)(R)Ru–{CNSiH₂C(SiMe₃)₃}] (**5a**: R = Me, 76 %, **5b**: R = Ph, 73 %; Scheme 1). The ¹H NMR spectrum of **5a** shows the signals for



Scheme 1. Reactions of **1** with nitriles.

RuMe and SiH at $\delta = 0.49$ and 4.71 ppm ($^1J_{\text{SiH}} = 228.0$ Hz), and the ¹³C NMR spectrum exhibits the signals for CN and CO at $\delta = 196.8$ and 207.0 ppm, respectively. In the IR spectrum of **5a**, the stretching vibrations for CO and CN are observed at 1923 and 2013 cm^{−1}, respectively.

Interestingly, at the early stage of this reaction, an iminoacyl complex with an agostic interaction at one of the Si–H bonds, [Cp*(CO)Ru{C(R)=NSiH₂C(SiMe₃)₃}] (**6a**: R = Me, **6b**: R = Ph), was detected as an intermediate by NMR spectroscopy (see Scheme 1). Complex **6a** shows the signals for the η^2 -coordinated Si–H moiety upfield in the ²⁹Si NMR spectrum ($\delta = -85.2$ ppm, 223 K) and also in the ¹H NMR spectrum ($\delta = -10.53$ ppm), and the large coupling constant $^1J_{\text{SiH}}$ (72.8 Hz) observed in the latter is consistent with η^2 -Si–H coordination (a typical range is 20–70 Hz).^[6,10] The structure of **6a** was confirmed by the X-ray crystal-structure analysis of the isolated η^5 -C₅Me₄Et derivative, **6c** (Experimental Section, Figure 2).^[7] The Si1 atom is in a tetrahedral environment, not counting the Ru1–Si1 bond, and is thus sp³-hybridized. The Si1–H2 bond length (1.71(3) Å) indicates a significant Si–H bond elongation that suggests substantial Ru (d_{π}) to Si–H (σ^*) back-donation (the typical η^2 -Si–H bond length is in the range of 1.6–1.9 Å).^[10b] The Ru1–Si1

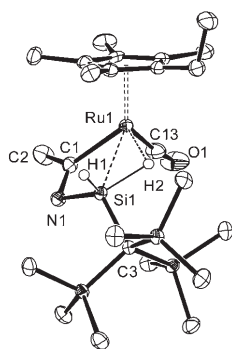
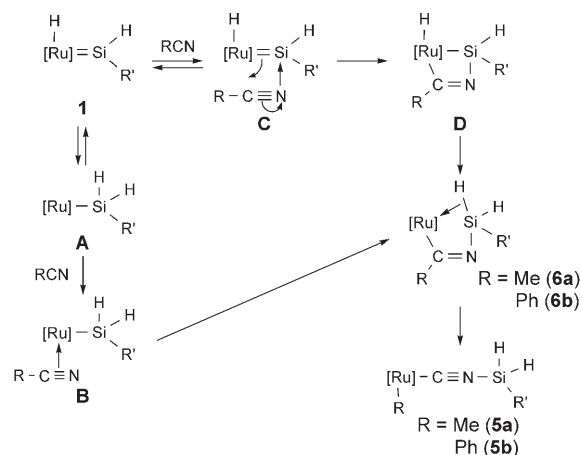


Figure 2. ORTEP drawing of **6c** (thermal ellipsoids set at 50% probability). Hydrogen atoms attached to carbon atoms omitted for clarity.

bond length is 2.5563(7) Å which is slightly longer than a normal Ru–Si single bond.^[11]

Possible mechanisms for the reaction of **1** with nitriles are depicted in Scheme 2. This reaction is closely related to the C–C bond activation of nitriles by rhodium and iron silyl

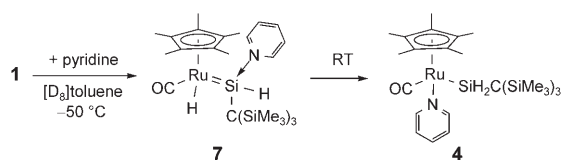


Scheme 2. Reaction mechanisms for the reaction of **1** with nitriles. [Ru] = {Cp*Ru(CO)}, R' = C(SiMe₃)₃. See text for details.

complexes, giving silylisocyanide complexes, reported recently by Brookhart et al. and Nakazawa et al.^[12] There are two possible mechanisms for the formation of intermediate **6** from **1**: one possibility proceeds through 1,2-H migration to give 16-electron silyl complex **A**, coordination of a nitrile molecule to ruthenium to give **B**, silyl ligand migration to nitrogen, and η^2 -coordination of an Si–H bond. This mechanism is analogous to the Brookhart–Nakazawa mechanism that produces a metal–C≡N three-membered-ring iminoacyl complex.^[12] In contrast, the other mechanism starts from the coordination of a nitrile molecule to the silylene silicon to generate **C**. Then, [2+2] cycloaddition, giving four-membered metallacycle **D**, followed by partial reductive elimination of the Si–H bond forms **6**. From **6**, decomplexation of the η^2 -Si–H bond and intramolecular C–C bond oxidative addition leads to **5**.

To determine which intermediate, **B** or **C**, is formed in the initial step, we monitored the reaction of **1** with pyridine by ¹H and ²⁹Si NMR spectroscopy. The reaction proceeded at −50 °C to afford a base-stabilized silylene complex [Cp*(CO)(H)Ru=Si(py)(H){C(SiMe₃)₃}] (**7**), which has a ²⁹Si NMR signal at $\delta = 98.6$ ppm. This chemical shift is characteristic for base-stabilized silylene complexes. Subsequent warming of this mixture to room temperature resulted in conversion of **7** into silyl complex **4** (Scheme 3). This result implies that, in the reaction of **1** with nitriles, the initial step is the formation of base-stabilized silylene complex **C**. From **C**, either [2+2] cycloaddition to form **D** or conversion into **B** could occur to produce **6**. However, at present, we cannot determine conclusively which mechanism is operative.

Importantly, there is another possible reaction from **C**, that is, the migration of the hydrido ligand from ruthenium to the coordinated nitrile carbon to result in hydrosilylation.



Scheme 3. Reaction of **1** with pyridine.

This type of reaction is indeed a dominant process in the reaction of tungsten complex **2** with nitriles, but surprisingly it was not observed in the case of ruthenium complex **1**. To clarify the reason for this difference, the mechanistic studies on the reaction of hydrido(hydrosilylene) complexes with nitriles and other polar unsaturated organic compounds are in progress.

Experimental Section

All manipulations were conducted in an atmosphere of dry argon or nitrogen by employing either standard Schlenk techniques or a glovebox.

1: Hexane (6 mL) was added to **4** (171 mg, 0.283 mmol) and BPh₃ (69 mg, 0.28 mmol) and the mixture was stirred for 4 h at room temperature. After 4 h, crystals of (py)BPh₃ were separated off by filtration and the filtrate was evaporated under vacuum to give an orange residue. Pentane (ca. 7 mL) was added to the residue, the mixture was cooled to −30 °C, and the precipitate (py)BPh₃ was filtered off by a membrane filter. The filtrate was concentrated under vacuum, and the residue was recrystallized from pentane (ca. 2 mL) at −30 °C to afford **1** as orange crystals in 71% yield (106 mg, 0.202 mmol). ¹H NMR (300 MHz, C₆D₆): δ = −11.19 (br s, 1H, RuH), 0.38 (s, 27H, SiMe₃), 1.87 (s, 15H, Cp*), 9.14 ppm (br s, ¹J_{SiH} = 136.9 Hz, 1H, SiH). ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ = 4.2 (SiMe₃), 11.1 (C₅Me₃), 29.2 (C(SiMe₃)₃), 79.5 (C₅Me₃), 210.4 ppm (CO). ²⁹Si{¹H} NMR (59.6 MHz, C₆D₆): δ = −4.1 (SiMe₃), 337.5 (SiH). IR (KBr pellet): $\tilde{\nu}$ = 2021 (m, ν_{SiH}), 1973 (vs, ν_{CO}), 1923 cm^{−1} (s, ν_{RuH}). Elemental analysis (%) calcd for C₂₁H₄₄OSi₄Ru: C 47.95, H 8.43; found: C 47.82, H 8.60.

6c: As soon as acetonitrile (8.8 μ L, 0.17 mmol) was added to a hexane solution of [(η^5 -C₅Me₄Et)(CO)(H)Ru=Si(H)[C(SiMe₃)₃]] (**1b**; 61 mg, 0.11 mmol), volatile components were removed under vacuum. Hexane (1 mL) was added to the residue, and toluene was added dropwise until the precipitate dissolved. The solution was cooled to −30 °C for two days to give **6c** as yellow crystals in 41% yield (26 mg, 0.045 mmol). ¹H NMR (300 MHz, [D₈]toluene): δ = −10.60 (d, ²J_{HH} = 9.2 Hz, ¹J_{SiH} = 74.7 Hz, 1H, η^2 -SiH), 0.43 (s, 27H, SiMe₃), 0.83 (t, ³J_{HH} = 7.7 Hz, 3H, CH₂CH₃), 1.60 (s, 6H, C₅Me₄Et), 1.65 (s, 6H, C₅Me₄Et), 2.12 (q, ³J_{HH} = 7.7 Hz, 2H, CH₂CH₃), 2.44 (s, 3H, NMe), 4.80 ppm (d, ²J_{HH} = 9.2 Hz, ¹J_{SiH} = 225.0 Hz, 1H, SiH). ²⁹Si{¹H} NMR (59.6 MHz, [D₈]toluene, 243 K): δ = −86.5 (SiH), −0.1 ppm (SiMe₃). MS (EI, 70 eV) 581 (*M*⁺, 32), 566 (*M*⁺−CH₃, 100), 522 (*M*⁺−CO−H, 5), 534 (*M*⁺−3CH₃−2H, 48), 73 (SiMe₃, 24). Elemental analysis (%) calcd for C₂₄H₄₉NOSi₄Ru: C 49.61, H 8.50, N 2.41; found: C 49.82, H 8.24, N 2.55.

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- [7] **1:** orthorhombic, *P*2₁2₁1; *a* = 11.3837(3), *b* = 13.7325(6), *c* = 17.3339(7) Å, *V* = 2709.7(2) Å³, *Z* = 4; C₂₁H₄₄OSi₄Ru, *T* = 150(2) K, 23179 reflections, 6038 independent reflections (*R*_{int} = 0.0894), *R*1 = 0.0621 (*I* > 2σ(*I*)), *wR*2 = 0.1110; μ = 0.765 mm^{−1}. **6c:** triclinic; *P* $\bar{1}$; *a* = 9.1065(4), *b* = 11.8594(5), *c* = 14.6238(8) Å, α = 72.630(3), β = 85.785(3), γ = 81.268(2)°, *Z* = 2; C₂₄H₄₉NOSi₄Ru, *T* = 150(2) K, 13827 reflections, 6572 independent reflections (*R*_{int} = 0.0302), *R*1 = 0.0289 (*I* > 2σ(*I*)), *wR*2 = 0.0975; μ = 0.704 mm^{−1}; refinement by full-matrix least-squares methods on *F*². The positions of the Si–H and the Ru–H hydrogen atoms were located in the difference Fourier electron-density map and were refined with isotropic thermal parameters. CCDC-653361 (**1**) and 653364 (**6c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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