

Tungsten–Silylene Complexes

Hydrido(hydrosilylene)tungsten Complexes with Strong Interactions between the Silylene and Hydrido Ligands**

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The chemistry of transition-metal–silylene complexes has been extensively studied owing to their hypothetically important roles in many catalytic processes.^[1] Since the late 1980s a number of base-stabilized and base-free silylene complexes have been synthesized and characterized.^[1–11] Among these complexes, those that bear H atoms on the silylene ligand are particularly interesting because the Si–H bond could diversify the reactivity of the M=Si bond through its possible reactions, such as α -elimination, oxidative addition, and hydrosilylation. However, donor-free silylene complexes of this type only became known quite recently. Youngs et al. reported the generation of the cationic silylene complex $[(\text{Et}_3\text{P})_3(\text{H})_2\text{Ir}=\text{Si}(\text{H})(2,6\text{-Mes}_2\text{C}_6\text{H}_3)]\text{B}(\text{C}_6\text{F}_5)_4$ (Mes = 2,4,6-trimethylphenyl),^[9] and Tilley et al. reported the formation of neutral $[\{\text{PhB}(\text{CH}_2\text{PPh}_2)_3\}(\text{H})_2\text{Ir}=\text{Si}(\text{H})(2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2)]$ and its interesting reactivity.^[11] The isolation and structural characterization of such complexes have not yet been achieved.

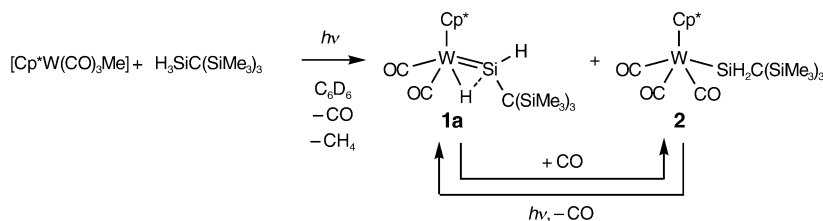
We previously reported that the photoreaction of $[\text{Cp}^*\text{Fe}(\text{CO})_2\text{SiMe}_3]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with a relatively bulky $\text{H}_3\text{SiR}'$ ($\text{R}' = t\text{Bu}$, $(\text{CMe}_2)_2\text{H}$) gave mononuclear dihydrosilyliron complexes $[\text{Cp}^*\text{Fe}(\text{CO})_2\text{SiH}_2\text{R}']$.^[12] We have now applied this methodology to tungsten complexes and the much bulkier $\text{H}_3\text{SiC}(\text{SiMe}_3)_3$ ligand to synthesize the hydrido(hydrosilylene) complexes $[\text{Cp}'(\text{CO})_2(\text{H})\text{W}=\text{Si}(\text{H})\text{-C}(\text{SiMe}_3)_3]$ (**1a**, $\text{Cp}' = \text{Cp}^*$; **1b**, $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_4\text{Et}$). Here

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[**] This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan (Grants-in-Aid for Scientific Research Nos. 14204065, 14078202, and 14044010).

we report the synthesis, isolation, and full characterization of **1a**, **1b**, a CO adduct of **1a**, namely $[\text{Cp}^*(\text{CO})_3\text{WSiH}_2\text{-C}(\text{SiMe}_3)_3]$ (**2**), and the stoichiometric hydrosilylation of acetone by **1a**. The X-ray crystal structure of **1b** and theoretical calculations on a model compound of **1** are also presented.

Irradiation (24 min) of a solution of $[\text{Cp}^*\text{W}(\text{CO})_3\text{Me}]$ and $\text{H}_3\text{SiC}(\text{SiMe}_3)_3$ in C_6D_6 in a sealed pyrex NMR tube with a 450 W medium-pressure Hg lamp produced an approximately 1:1 mixture of silylene complex **1a** and silyl complex **2** in a photostationary state (Scheme 1). When this solution was kept in the sealed tube at room temperature, **1a** reacted with



Scheme 1. Photoreaction of $[\text{Cp}^*\text{W}(\text{CO})_3\text{Me}]$ with $\text{H}_3\text{SiC}(\text{SiMe}_3)_3$.

CO that was produced during photolysis and was completely converted to **2** after 4 days. Complex **1a** was isolated as a single product in 62 % yield when the irradiation was performed with periodic removal of CO gas from the irradiated solution. Similarly, the $\eta^5\text{-C}_5\text{Me}_4\text{Et}$ analogue **1b** was isolated in 44 % yield. Isolated **1a** reacted quantitatively with CO gas at room temperature to give **2**. Conversely, **2** was completely converted to **1a** by irradiation and periodic removal of CO gas.

The ^{29}Si NMR spectrum (C_6D_6) of **1a** exhibits two signals for the silylene and silyl ligands at $\delta = 275.3$ and -3.6 ppm, respectively. The large downfield shift of the silylene signal, which is comparable to that of reported hydrido(hydrosilylene) complexes such as $[(\text{Et}_3\text{P})_3(\text{H})_2\text{Ir}=\text{Si}(\text{H})(2,6\text{-Me}_2\text{C}_6\text{H}_3)]\text{B}(\text{C}_6\text{F}_5)_4$ ($\delta = 239.3$ ppm),^[11] suggests that the silicon atom of the silylene ligand in **1a** is essentially sp^2 hybridized. The ^1H NMR spectrum (C_6D_6) of **1a** shows signals for SiH and WH groups at $\delta = 10.39$ ($^1J_{\text{SiH}} = 154.9$ Hz) and -10.67 ppm ($^1J_{\text{WH}} = 64.9$ Hz), respectively. The significant downfield shift of the SiH signal is consistent with sp^2 hybridization of the silicon atom. Importantly, the $^2J_{\text{SiH}}$ coupling constant (28.6 Hz) observed for the WH signal implies the existence of direct interaction between the hydrido and silylene ligands.^[13] Note that there is no indication of such interaction for $[\{\text{PhB}(\text{CH}_2\text{PPh}_2)_3\}(\text{H})_2\text{Ir}=\text{Si}(\text{H})\text{R}]$,^[9] $[(\text{Et}_3\text{P})_3(\text{H})_2\text{Ir}=\text{Si}(\text{H})\text{R}']\text{B}(\text{C}_6\text{F}_5)_4$,^[11] and the related tungsten complexes $[\text{Cp}^*(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)(\text{H})_2\text{W}=\text{SiMe}_2]\text{B}(\text{C}_6\text{F}_5)_4$ ^[4] and $[\text{Cp}^*(\text{CO})_2(\text{H})\text{W}=\text{SiPh}_2(\text{py})]$ (py = pyridine).^[5] In the ^{13}C NMR spectrum, **1a** shows a single resonance for carbonyl groups at $\delta = 231.8$ ppm at room temperature, while two signals are observed at $\delta = 233.0$ and 235.3 ppm at 183 K in $[\text{D}_8]\text{toluene}$ ($\Delta G_{213\text{K}}^\ddagger = 41$ kJ mol $^{-1}$, determined by the coalescence-point method). This result indicates that rapid exchange of carbonyl groups occurs in **1a** at room temperature. In the IR spectrum, the ν_{CO} bands for **1a** (1928 and

1853 cm^{-1}) appear at higher energy than those of $[\text{Cp}^*(\text{CO})_2(\text{H})\text{W}=\text{SiPh}_2(\text{py})]$ (1892 and 1806 cm^{-1}).^[5] This is apparently attributable to stronger back-donation to the silylene ligand in **1a**, which leads to weaker back-donation to the carbonyl ligands. The ν_{SiH} band appears at 2052 cm^{-1} . A weak and broad absorption observed at 1589 cm^{-1} can be assigned to the WH group, interaction of which with the silylene ligand dramatically reduces the strength of the W–H bond.^[14]

The solid-state structure of **1b** was determined by X-ray crystal structure analysis (Figure 1).^[15] Selected bond lengths and angles are listed in Table 1. The tungsten atom in **1b** adopts a distorted four-legged piano-stool structure, in which the hydrido and silylene ligands occupy the mutually *cis* positions. The W–Si(1) bond length (2.3703(11) Å) is shorter than those of known silyltungsten complexes (2.469–2.653 Å).^[16] This length is even shorter than that of the donor-free silyl(silylene)tungsten complex $[\text{Cp}^*\text{W}(\text{CO})_2(=\text{SiMe}_2)(\text{SiMe}_3)]$ (2.3850(12) Å),^[7] but somewhat longer than that of

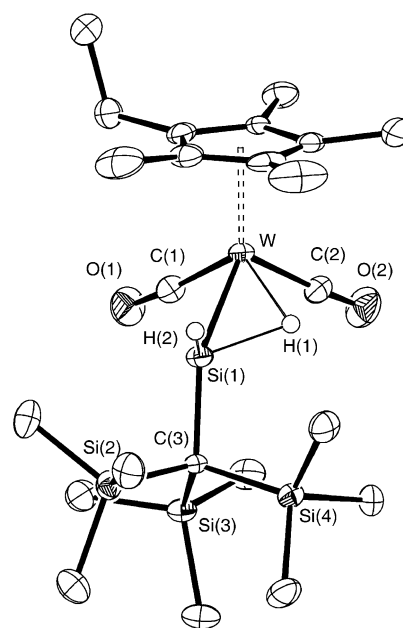


Figure 1. ORTEP plot of **1b**. Thermal ellipsoids are drawn at the 50 % probability level.

cationic $[\text{Cp}^*(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)(\text{H})_2\text{W}=\text{SiMe}_2]\text{B}(\text{C}_6\text{F}_5)_4$ (2.358(2) and 2.354(3) Å).^[4] The W–H bond is oriented toward the empty p orbital on the silicon atom of the silylene ligand. Although it is generally difficult to discuss M–H and Si–H interactions on the basis of X-ray structures, the W–H(1) and Si(1)–H(1) distances of 1.82(7) Å and 1.71(6) Å, respectively, in **1b** are both within the range in which a bonding interaction between two atoms exists.^[13] The Si(1)–W–H(1) and W–Si(1)–H(1) angles are 46(2) and 50(2)°, respectively. These angles and the W–H and Si–H distances

Table 1: Selected bond lengths [Å] and angles [°] for the X-ray crystal structure of **1b** and the energy-minimized structure of **1'**.

	1b	1'
W–Si(1)	2.3703(11)	2.377
W–H(1)	1.82(7)	1.85
Si(1)–H(1)	1.71(6)	1.71
Si(1)–H(2)	1.54(7)	1.50
W–C(1)	1.950(5)	1.97
W–C(2)	1.964(5)	1.98
Si(1)–W–H(1)	46(2)	46
W–Si(1)–H(1)	50(2)	51
W–Si(1)–C(3)	141.4(1)	135
W–Si(1)–H(2)	110(3)	121

in **1b** strongly indicate the existence of significant interligand interaction between the silylene and the hydrido ligands. Nevertheless, pyramidalization of the Si(1) atom is very small; the Si(1), W, H(2), and C(3) atoms are almost coplanar, and the sum of the valence angles around Si(1) excluding H(1) is 357(3)°. Therefore, **1** has an unprecedented structure in which a hydrido ligand bridges the W=Si bond.

This structural view of **1** was well reproduced by molecular orbital calculations. A DFT calculation at the B3LYP level was performed for model complex [Cp(CO)₂(H)W=Si(H){C(SiH₃)₃}] (**1'**).^[17] The structural parameters of the energy-minimized structure of **1'** are in good agreement with those of the X-ray crystal structure of **1b** (Table 1). The overlap populations, Wiberg bond indexes,^[18a] and NLMO/NPA bond orders^[18b] all indicate a significant interaction between the H atom of the WH group and the Si atom of the silylene ligand; for example, NLMO/NPA bond orders: 1.518 for W–Si, 0.511 for W–μ-H, and 0.476 for Si–μ-H. These data are rationalized by the existence of two bonding interactions, that is, the normal two-centered, two-electron (2c–2e) W–Si bond and the 3c–2e W–H–Si bond in the W–H–Si moiety of **1'**, according to NBO analysis.^[18c]

Complex **1a** reacted with one molar equivalent of acetone in C₆D₆ at room temperature over 1 h to give mainly the hydrosilylation product [Cp*(CO)₂(H)W=Si(OCHMe₂)-{C(SiMe₃)₃}] (**3**) together with a few unidentified products. Complex **3** was characterized by ¹H, ¹³C, and ²⁹Si NMR spectroscopy.^[19] This result suggests a possible role of the hydrido(hydrosilylene) complex as an intermediate in the hydrosilylation of ketones with trihydrosilane. We are now investigating **1a** as a catalyst for hydrosilylation reaction.

In summary, **1a** and **b** are the first isolated and structurally characterized hydrido(hydrosilylene) complexes. They exhibit a strong interligand interaction between the hydrido and silylene ligands. Complex **1a** hydrosilylates acetone at room temperature to give **3**. Further studies on the reactivity of **1** are in progress.

Experimental Section

1a: A degassed solution of [Cp*W(CO)₃Me] (100 mg, 0.239 mmol) and H₃SiC(SiMe₃)₃ (70 mg, 0.27 mmol) in hexane in a pyrex sample tube with a teflon vacuum valve was irradiated with a 450 W medium-pressure Hg lamp for 2 h at 5 °C. The reaction mixture was degassed at

15 min intervals by a freeze–pump–thaw cycle on a vacuum line. The reaction mixture was filtered through a membrane filter, and volatile substances were removed from the filtrate. The residue was washed with cold hexane (0.3 mL × 3) and dried to give 98 mg (0.15 mmol, 64 %) of **1a** as orange crystals. ¹H NMR (300 MHz, C₆D₆): δ = –10.67 (d, 1H, ¹J_{WH} = 64.9, ²J_{SiH} = 28.6, ³J_{HH} = 1.8 Hz, WH), 0.37 (s, 27H, SiMe), 1.90 (s, 15H, C₅Me₅), 10.39 ppm (d, 1H, ¹J_{SiH} = 154.9, ²J_{WH} = 13.3, ³J_{HH} = 1.8 Hz, SiH). ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ = 3.9 (SiMe), 11.4 (C₅Me₅), 24.0 (CSiMe₃), 102.7 (C₅Me₅), 232.4 ppm (CO). ²⁹Si{¹H} NMR (59.6 MHz, C₆D₆): δ = –3.6 (SiMe), 275.3 ppm (WSi, ¹J_{WSi} = 109.9 Hz). IR (C₆D₆): ν̃ = 2052 (ν_{SiH}), 1928, 1853 (ν_{CO}), 1589 cm^{–1} (ν_{WH}). Elemental analysis (%) calcd for C₂₂H₄₄O₂Si₄W₁: C 41.50, H 6.96; Found: C 41.32, H 6.86.

1b: Complex **1b** was obtained as orange crystals by a procedure similar to that for **1a** from [(η⁵-C₅Me₄Et)W(CO)₃Me] (240 mg, 0.555 mmol) and H₃SiC(SiMe₃)₃ (70 mg, 0.56 mmol). Yield: 160 mg (0.246 mmol, 44 %). ¹H NMR (300 MHz, C₆D₆): δ = –10.67 (d, 1H, ¹J_{WH} = 65.0, ²J_{SiH} = 28.3, ³J_{HH} = 1.7 Hz, WH), 0.38 (s, 27H, SiMe), 0.85 (t, 3H, ³J_{HH} = 7.7 Hz, C₅Me₄CH₂CH₃), 1.90 (s, 6H, C₅Me₄Et), 1.95 (s, 6H, C₅Me₄Et), 2.30 (q, 2H, ³J_{HH} = 7.7 Hz, C₅Me₄CH₂CH₃), 10.42 ppm (d, 1H, ¹J_{SiH} = 155.1, ²J_{WH} = 13.7, ³J_{HH} = 1.7 Hz, SiH). ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ = 3.8 (SiMe), 10.9 (C₅Me₄Et), 11.2 (C₅Me₄Et), 16.4 (C₅Me₄Et), 20.0 (C₅Me₄Et), 23.9 (CSiMe₃), 102.0 (C₅Me₄Et), 103.1 (C₅Me₄Et), 108.4 (C₅Me₄Et), 232.1 ppm (CO). ²⁹Si{¹H} NMR (59.6 MHz, C₆D₆): δ = –3.6 (SiMe), 275.1 ppm (WSi, ¹J_{WSi} = 109.9 Hz). IR (C₆D₆): ν̃ = 2052 (ν_{SiH}), 1928, 1853 (ν_{CO}), 1589 cm^{–1} (ν_{WH}). Elemental analysis (%) calcd for C₂₃H₄₆O₂Si₄W₁: C 42.45, H 7.12; Found: C 42.43, H 7.01.

2: A solution of [Cp*W(CO)₃Me] (100 mg, 0.239 mmol) and H₃SiC(SiMe₃)₃ (70 mg, 0.266 mmol) in hexane was irradiated for 2 h at 5 °C in a sealed pyrex tube. After the sample tube had stood for 60 h at room temperature, the reaction mixture was filtered through a membrane filter, and volatile substances were removed from the filtrate. The residue was washed with cold hexane (0.3 mL × 3) and dried to give 79 mg (0.12 mmol, 50 %) of **2** as orange crystals. ¹H NMR (300 MHz, C₆D₆): δ = 0.49 (s, 27H, SiMe), 1.58 (s, 15H, C₅Me₅), 4.37 ppm (s, 2H, SiH, ¹J_{SiH} = 179.3 Hz). ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ = –5.0 (CSiMe₃), 5.43 (SiMe), 9.6 (C₅Me₅), 102.2 (C₅Me₅), 223.9 ppm (CO). ²⁹Si{¹H} NMR (59.6 MHz, C₆D₆): δ = –27.2 (WSi), 0.80 ppm (SiMe). IR (KBr pellet): ν̃ = 2096 (ν_{SiH}), 1982, 1903, 1888 cm^{–1} (ν_{CO}). Elemental analysis (%) calcd for C₂₃H₄₄O₃Si₄W₁: C 41.55, H 6.67; Found C 41.85, H 6.69.

Received: July 15, 2003

Revised: September 22, 2003 [Z52383]

Keywords: hydrido ligands · hydrosilylation · silicon · silylene complexes · tungsten

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- [14] The calculated W–H stretching frequency (1525 cm^{-1}) is close to the experimental value. Accordingly, the ν_{SiD} and ν_{WD} bands of $[\text{Cp}^*(\text{CO})_2(\text{D})\text{W}=\text{Si}(\text{D})\{\text{C}(\text{SiMe}_3)_3\}]$ appear at 1481 and 1142 cm^{-1} , respectively.
- [15] **1b**: monoclinic; $P2_1/n$; $a = 15.9541(5)$, $b = 11.8021(3)$, $c = 17.2847(5)\text{ \AA}$, $\beta = 114.6906(14)^\circ$, $V = 2957.02(15)\text{ \AA}^3$, $Z = 4$; $\text{C}_{23}\text{H}_{46}\text{O}_2\text{Si}_4\text{W}$, $T = 150(2)\text{ K}$, 24833 reflections, 6358 independent reflections ($R_{\text{int}} = 0.0555$), $R1 = 0.0297$ ($I > 2\sigma(I)$), $wR2 = 0.0875$; $\mu = 4.085\text{ mm}^{-1}$; refinement by full-matrix least-squares methods on F^2 . The positions of the hydrogen atoms of the SiH and the WH groups were located in the Fourier-difference electron-density map and were refined with isotropic thermal parameters. CCDC-214274 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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- [19] Spectral data of **3**: ^1H NMR (300 MHz, C_6D_6): $\delta = -6.12$ (s, 1H, WH, $^1J_{\text{WH}} = 56.0\text{ Hz}$, $^2J_{\text{SiH}} = 34.0\text{ Hz}$), 0.46 (s, 27H, SiMe), 1.39 (d, $^3J_{\text{HH}} = 6.3\text{ Hz}$, 6H, OCHMe_2), 1.94 (s, 15H, C_5Me_5), 4.84 ppm (sept, $^3J_{\text{HH}} = 6.3\text{ Hz}$, 1H, OCHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta = 6.8$ (SiMe), 11.5 (C_5Me_5), 25.8 (OCHMe_2), 33.6 (CSiMe_3), 68.7 (SiOCHMe_2), 100.9 (C_5Me_5), 225.6 (CO). $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.6 MHz, C_6D_6): $\delta = -2.1$ (SiMe), 229.2 ppm (WSi, $^1J_{\text{WSi}} = 130.8\text{ Hz}$).