

Addition of HCl to a Base-Stabilized Hydrido(silylene)tungsten Complex and Reactivity of the Adduct toward LiAlH₄

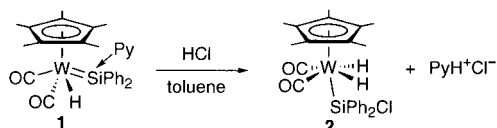
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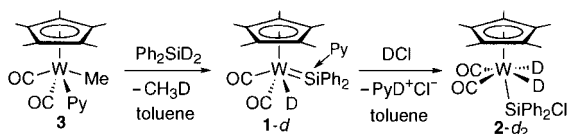
The reaction of *cis*-Cp*(CO)₂HW=SiPh₂·Py (**1**, Py = pyridine) with HCl gave an adduct Cp*(CO)₂H₂WSiPh₂Cl (**2**). Treatment of **2** with excess LiAlH₄ afforded an anionic complex Li[*cis*-Cp*(CO)₂HWSiHPh₂] (**4**), and the same product was obtained by the reaction of **1** with LiAlH₄.

Recent extensive studies on silylene complexes have revealed their high reactivities toward the addition of polar molecules such as alcohols and water.¹ However, the addition of hydrogen halide to a silylene complex, one of fundamental reactions expected for the polarized metal–silicon double bond, has not been reported so far. We have recently reported the synthesis of the base-stabilized hydrido(silylene) complex *cis*-Cp*(CO)₂HW=SiR₂·Py and its novel reactivity toward a secondary silane leading to a silylene exchange reaction.² Here we report for the first time the addition of hydrogen chloride to the base-stabilized silylene complex to afford a stable adduct. The reactivities of the HCl adduct and the silylene complex toward LiAlH₄ are also described.

The silylene complex *cis*-Cp*(CO)₂HW=SiPh₂·Py (**1**)² reacted rapidly with HCl (ca. 2 equiv) in toluene to afford the adduct Cp*(CO)₂H₂WSiPh₂Cl (**2**),³ which was isolated in 72% yield as an air-stable pale yellow solid after filtration of the mixture to remove pyridinium chloride and concentration of the filtrate. The orientation of the addition is in accordance with the polarization of M^{δ-}=Si^{δ+} shown by theoretical studies.⁴

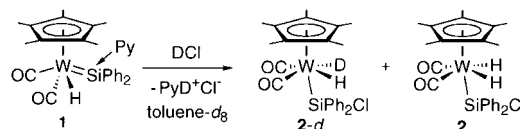


The ¹H NMR spectrum of **2** exhibited a broad WH signal at –6.35 ppm at room temperature, and on cooling to –40 °C, it became sharp enough to detect tungsten satellites with ¹J_{WH} = 58.6 Hz and silicon satellites with ²J_{SiWH} = 18.3 Hz.⁵ This ²J_{SiWH} value is close to the lower limit of the known J_{SiH} range (22–98 Hz) for η²-Si–H bonds,⁶ and might suggest a weak Si··H interaction in **2**. In the IR spectrum of **2**, a weak absorption assigned to ν_{WH} band was observed at 1848 cm^{–1}. The assignment is supported by the disappearance of the absorption and the appearance of a new absorption at 1323 cm^{–1} in the IR spectrum of **2-d**, which was synthesized by the reaction of the pyridine complex **3**² with Ph₂SiD₂ followed by DCl addition to the resulting deuteride complex **1-d**. The ratio of the absorption frequencies observed for **2** and **2-d** is very close to the calculated value.



In order to get information on the interaction between the two

hydrides in **2**, Cp*(CO)₂HDWSiPh₂Cl (**2-d**) was synthesized by the reaction of **1** with DCl (ca. 2 equiv), where **2** was also formed (**2-d**:**2** ≈ 1:0.6).⁷ The hydride signal of **2-d** (–6.45 ppm) was observed as a sharp singlet (ω_{1/2} ≈ 5 Hz) without HD coupling along with that of **2** (–6.42 ppm) in the ¹H NMR spectrum at –60 °C, indicating that **2** is not a η²-H₂ complex.⁸



The X-ray crystal structure of **2** is shown in Figure 1,⁹ which reveals a distorted octahedral structure with two CO ligands arranged almost symmetrically with respect to the plane defined by Cp*(centroid)–W1–Si1. Interesting structural characteristic is the tilting of the W–Si bond toward two hydride ligands as shown by the Cp*(centroid)–W1–Si1 angle of 153.8°. This tilting might be due to the weak Si··H interaction suggested by the ²J_{SiWH} value, although the repulsive interaction between the bulky silyl group and the carbonyl ligands is also conceivable. Recent studies on chlorosilyl(hydrido) complexes by Nikonov have revealed an interesting interaction between a metal hydride and a chlorosilyl group, interligand hypervalent interaction (IHI), where the overlap of a M–H bonding orbital and a Si–Cl antibonding orbital causes a short Si–H contact associated with short M–Si and long Si–Cl bonds.¹⁰ This interaction requires the trans orientation of the M–H bond to the Si–Cl bond, and interestingly, such an orientation is seen for the W1–H1 and Si1–Cl1 bonds in **2**. It is found, however, that **2** is devoid of this type of interaction, judging from the W1–Si1 (2.5604(9) Å) and Si1–Cl1 (2.135(1) Å) bond lengths, which are both within the respective normal ranges for W–Si (2.533–2.633 Å)¹¹ and Si–Cl (2.094–2.148 Å)^{10b} bond lengths in non-interacting systems. Considering the finding that a more electron donating

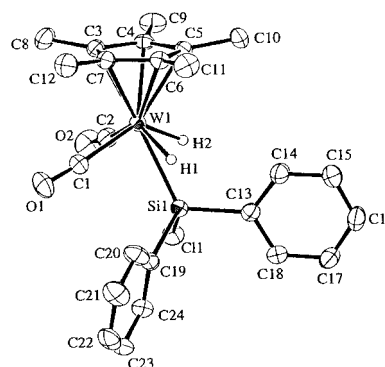
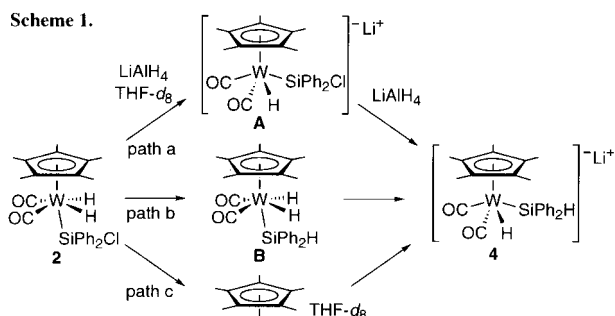


Figure 1. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms except for W–H atoms are omitted for clarity. Selected bond length (Å) and angles (deg): W1–Si1, 2.5604(9); W1–Cl1, 1.994(4); W1–C2, 1.979(4); W1–H1, 1.70(4); W1–H2, 1.49(3); Si1–W1–Cl1, 82.4(1); Si1–W1–C2, 83.8(1); C1–W1–C2, 81.7(2).

phosphine favors IHI in complexes of the type $\text{Cp}^*(\text{PR}_3)\text{RuH}_2\text{SiR}_2\text{Cl}$,^{10b} the existence of π -acidic CO ligands probably disfavors IHI in **2**.

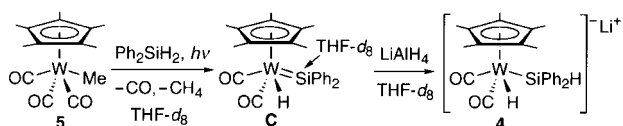
When **2** was treated with excess LiAlH_4 in THF-d_8 to reduce the Si-Cl bond, a rapid reaction took place to give the anionic complex $\text{Li}[\text{cis-Cp}^*(\text{CO})_2\text{HWSiHPh}_2]$ (**4**)³ (Scheme 1), showing WH and SiH signals at -7.16 ($^1J_{\text{WH}} = 73.6$ Hz) and 5.35 ($^1J_{\text{SiH}} = 160.1$ Hz) ppm, respectively, in the ^1H NMR spectrum. Its anionic character is supported by the 183 cm^{-1} difference in the average CO stretching frequencies between **4** (1867 and 1717 cm^{-1} , $\nu_{\text{av}} = 1792\text{ cm}^{-1}$) and the neutral complex **2** (2006 and 1944 cm^{-1} , $\nu_{\text{av}} = 1975\text{ cm}^{-1}$).

Scheme 1.



Possible mechanisms for the formation of **4** are shown in Scheme 1. Path a is a sequence of deprotonation of the tungsten hydride of **2** and chloride/hydride exchange in the resulting anionic intermediate **A**, and path b is the reversed combination of these two processes via **B**. The third pathway is E2 elimination to produce silylene complex **C** followed by hydride attack to the electrophilic silylene center of **C**. To get mechanistic information, the reaction was monitored by low-temperature ^1H NMR spectroscopy. Interestingly, the reaction slowly proceeded around -70°C to form an intermediate, which is characterized as the deprotonation product $\text{Li}[\text{cis-Cp}^*(\text{CO})_2\text{HWSiClPh}_2]$ (**A**)³ from the observation of WH (-8.03 ppm, $^1J_{\text{WH}} = 68.2$ Hz, 1H) and Cp^* (1.89 ppm, 15H) signals, and occurrence of the deprotonation is supported by detection of a signal at 4.56 ppm assigned to H_2 . The ^{29}Si signal is observed at 69.5 ppm at -60°C . When the temperature was raised above -45°C , the signals due to **A** decreased and those of the final product **4** became predominant.

Although the observation of the WH and Cp^* signals with an intensity ratio 1:15 for the intermediate is not inconsistent with the silylene complex **C**, such a possibility is ruled out by comparison of the spectroscopic data of the intermediate with those of **C** synthesized by photolysis of $\text{Cp}^*(\text{CO})_3\text{WMe}$ (**5**) and Ph_2SiH_2 in THF-d_8 , showing characteristic ^1H and ^{29}Si signals at -9.31 ppm (W-H) and 119.3 ppm (W=Si).³ These results clearly demonstrate that **4** is produced from **2** via path a.



Despite of the electrophilic nature of the silylene center of a silylene complex, a reactivity study of an isolated silylene complex toward a hydride reagent is rare. To our knowledge, the only preceeding example is the reaction of the cationic silylene complex $\text{Cp}^*(\text{PMe}_3)_2\text{Ru}=\text{SiPh}_2(\text{NCMe})^+$ with LiAlH_4 to form the neutral

hydrosilyl complex $\text{Cp}^*(\text{PMe}_3)_2\text{RuSiHPh}_2$.¹² In order to clarify a potential reactivity of the neutral silylene complex **C** toward hydride described above, the reaction of **C** with LiAlH_4 was examined. When LiAlH_4 was added to a THF-d_8 solution of **C**, the clean formation of **4** was shown by ^1H NMR spectroscopy. Similar reaction of **1** with LiAlH_4 also afforded **4**, and it was isolated as an air-sensitive white solid in 56% yield based on **5** from the photolysis of **5** and Ph_2SiH_2 in THF followed by treatment of the resulting silylene complex **C** with LiAlH_4 in ether. We are currently exploring the reactivity of **4** as a precursor to a variety of hydrido(hydrosilyl) tungsten complexes.

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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

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- Selected data: **2**: ^1H NMR (400 MHz, C_6D_6) δ 7.92–7.90 (m, 4H, Ph), 7.25–7.21 (m, 4H, Ph), 7.14–7.10 (m, 2H, Ph), 1.75 (s, 15H, Cp^*), -6.35 (br s, 2H, WH); ^{29}Si NMR (C_6D_6 , -60°C) δ 23.0; IR (toluene) $\nu_{\text{CO}} = 2006$ (s), 1944 (s) cm^{-1} ; Anal. Calcd for $\text{C}_{24}\text{H}_{27}\text{ClO}_2\text{SiW}$: C, 48.46; H, 4.57%. Found: C, 48.54; H, 4.77%. **4**: ^1H NMR (400 MHz, THF-d_8) δ 7.65 (dd, $J = 8.1, 1.6$ Hz, 4H, Ph), 7.01 (t, $J = 7.5$ Hz, 4H, Ph), 6.94 (tt, $J = 7.5, 1.6$ Hz, 2H, Ph), 5.35 (d, $J = 1.1$ Hz, $^1J_{\text{SiH}} = 160.1$ Hz, 1H, SiH), 1.92 (s, 15H, Cp^*), -7.16 (s, $^1J_{\text{WH}} = 73.6$ Hz, 1H, WH); ^{29}Si NMR (THF-d_8) δ 29.5; IR (toluene) = 1867 (s), 1717 (s) cm^{-1} . **A**: ^1H NMR (400 MHz, THF-d_8 , -60°C) δ 7.87 (s, 2H, Ph), 7.55 (s, 2H, Ph), 7.14 (s, 2H, Ph), 7.00 (s, 4H, Ph), 1.89 (s, 15H, Cp^*), -8.03 (s, $^1J_{\text{WH}} = 68.2$ Hz, 1H, WH); ^{29}Si NMR (THF-d_8 , -60°C) δ 69.5. **C**: ^1H NMR (400 MHz, THF-d_8) δ 7.39 (dd, $J = 8.1, 1.6$ Hz, 4H, Ph), 7.20–7.13 (m, 6H, Ph), 1.84 (s, 15H, Cp^*), -9.31 (s, $^1J_{\text{WH}} = 68.7$ Hz, 1H, WH); ^{29}Si NMR (THF-d_8) δ 119.3; IR (THF) $\nu_{\text{CO}} = 1896$ (s), 1809 (m) cm^{-1} . In each ^{13}C NMR spectrum of **4** and **A**, two CO signals are observed, indicating their cis configurations.
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- No decoalescence of the hydride signal was observed on cooling down to -80°C . In the low-temperature NMR experiments, very weak hydride signals of trace amounts of minor components were detected. Although their structures cannot be characterized, the interconversion between **2** and the minor components might cause the dynamic behavior.
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- The formation of **2-d**₂ is also suggested by the relative intensity of the Cp^* signal to the combined hydride signals of **2-d** and **2** (ca. 13:1), which is larger than a 10.9:1 ratio expected for a 1:0.6 mixture of **2-d** and **2** only. Although it is suggested that the H/D scrambling might be promoted by a catalytic amount of pyridine liberated from **1** by the fact that addition of pyridine to a mixture of **2** and **2-d**₂ in toluene- d_8 led to the rapid formation of **2-d**, detailed studies are required to clarify the mechanism.
- J_{HD} coupling constants for $\eta^2\text{-H}_2$ complexes are in the range of 20–34 Hz: R. H. Crabtree, "The Organometallic Chemistry of the Transition Metals," 3rd ed., John Wiley & Sons, Inc., New York (2001), p 73.
- Crystal data for **2**: $\text{C}_{24}\text{H}_{27}\text{ClO}_2\text{SiW}$, MW = 594.86, monoclinic, space group $P2_1/a$ (No. 14), $a = 16.067(3)$, $b = 8.901(2)$, $c = 16.856(3)$ Å, $\beta = 99.64(1)^\circ$, $V = 2376.7(8)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.662\text{ g/cm}^3$, $\mu(\text{Mo K}\alpha) = 50.45\text{ cm}^{-1}$, $R = 0.021$ ($R_w = 0.021$) for 5594 observed reflections [$I > 5.00\sigma(I)$]. All Hydrogens were found from successive D-Fourier syntheses, in which W-H atoms were assigned geometrically out of several peaks around W atom, and all hydrogens were refined isotropically. However, no detailed discussion about W-H bonds is made here because of the low accuracy.
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