Addition of HCl to a Base-Stabilized Hydrido(silylene)tungsten Complex and Reactivity of the Adduct toward $LiAlH_4$

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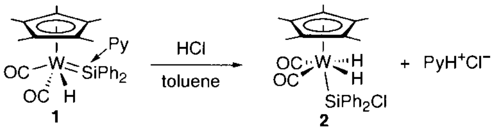
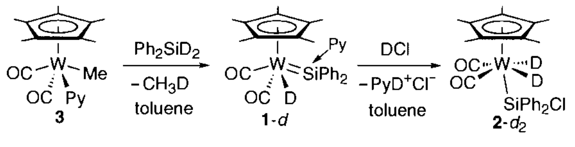
The reaction of *cis*-$Cp^*(CO)_2HW{=}SiPh_2{\cdot}Py$ (**1**, Py = pyridine) with HCl gave an adduct $Cp^*(CO)_2H_2WSiPh_2Cl$ (**2**). Treatment of **2** with excess $LiAlH_4$ afforded an anionic complex Li[*cis*-$Cp^*(CO)_2HWSiHPh_2$] (**4**), and the same product was obtained by the reaction of **1** with $LiAlH_4$.

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*-$Cp^*(CO)_2HW{=}SiR_2{\cdot}Py$ 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 $LiAlH_4$ are also described.

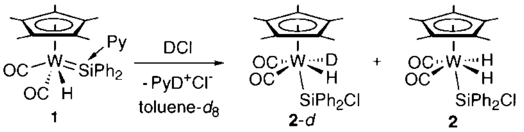
The silylene complex *cis*-$Cp^*(CO)_2HW{=}SiPh_2{\cdot}Py$ (**1**)[2] reacted rapidly with HCl (ca. 2 equiv) in toluene to afford the adduct $Cp^*(CO)_2H_2WSiPh_2Cl$ (**2**),[3] which was isolated in 72% yield as an air-stable pale yellow solid after filtration of the mixture to remove pyridinium chloride and concentration of the filtrate. The orientation of the addition is in accordance with the polarization of $M^{\delta-}{=}Si^{\delta+}$ 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 η^2-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_2, which was synthesized by the reaction of the pyridine complex **3**[2] with Ph_2SiD_2 followed by DCl addition to the resulting deuteride complex **1**-*d*. The ratio of the absorption frequencies observed for **2** and **2**-d_2 is very close to the calculated value.



In order to get information on the interaction between the two hydrides in **2**, $Cp^*(CO)_2HDWSiPh_2Cl$ (**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 ($\omega_{1/2}$ ≈ 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 η^2-H_2 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

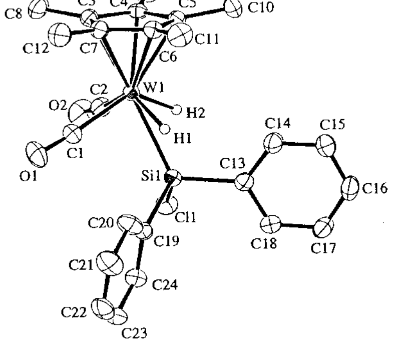
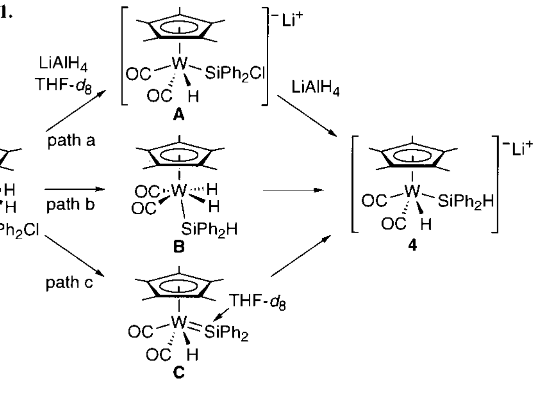


Figure 1. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms except for W–H atoms are omitted for clarity. Selected bond length (Å) and angles (deg): W1-Si1, 2.5604(9); W1-C1, 1.994(4); W1-C2, 1.979(4); W1-H1, 1.70(4); W1-H2, 1.49(3); Si1-W1-C1, 82.4(1);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

phosphine favors IHI in complexes of the type $Cp^*(PR_3)RuH_2SiR_2Cl$,[10b] the existence of π-acidic CO ligands probably disfavors IHI in **2**.

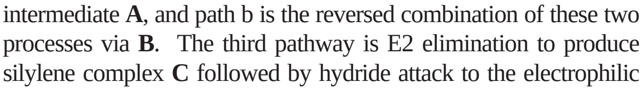
When **2** was treated with excess $LiAlH_4$ in THF-d_8 to reduce the Si–Cl bond, a rapid reaction took place to give the anionic complex Li[*cis*-$Cp^*(CO)_2HWSiHPh_2$] (**4**)[3] (Scheme 1), showing WH and SiH signals at –7.16 ($^1J_{WH}$ = 73.6 Hz) and 5.35 ($^1J_{SiH}$ = 160.1 Hz) ppm, respectively, 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}, ν_{av} = 1792 cm^{-1}) and the neutral complex **2** (2006 and 1944 cm^{-1}, ν_{av} = 1975 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 Li[*cis*-$Cp^*(CO)_2HWSiClPh_2$] (**A**)[3] from the observation of WH (–8.03 ppm, $^1J_{WH}$ = 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 $Cp^*(CO)_3WMe$ (**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 $Cp^*(PMe_3)_2Ru{=}SiPh_2(NCMe)^+$ with $LiAlH_4$ to form the neutral hydrosilyl complex $Cp^*(PMe_3)_2RuSiHPh_2$.[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

1 H. Wada, H. Tobita, and H. Ogino, *Organometallics*, **16**, 2200 (1997) and references therein.

2 H. Sakaba, M. Tsukamoto, T. Hirata, C. Kabuto, and H. Horino, *J. Am. Chem. Soc.*, **122**, 11511 (2000).

3 Selected data: **2**: ^1H NMR (400 MHz, C_7D_8) 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_7D_8, –60 °C) δ 23.0; IR (toluene) ν_{CO} = 2006 (s), 1944 (s) cm^{-1}; Anal. Calcd for $C_{24}H_{27}ClO_2SiW$: 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, $^1J_{SiH}$ = 160.1 Hz, 1H, SiH), 1.92 (s, 15H, Cp*), –7.16 (s, $^1J_{WH}$ = 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, $^1J_{WH}$ = 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, $^1J_{WH}$ = 68.7 Hz, 1H, WH); ^{29}Si NMR (THF-d_8) δ 119.3; IR (THF) ν_{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.

4 H. Jacobsen and T. Ziegler, *Inorg. Chem.*, **35**, 775 (1996).

5 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.

6 J. Y. Corey and J. Braddock-Wilking, *Chem. Rev.*, **99**, 175 (1999).

7 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.

8 J_{HD} coupling constants for η^2-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.

9 Crystal data for **2**: $C_{24}H_{27}ClO_2SiW$, MW= 594.86, monoclinic, space group $P2_1/a$ (No. 14), a = 16.067(3), b = 8.901(2), c = 16.856(3) Å, β = 99.64(1)°, V = 2376.7(8) Å^3, Z = 4, D_{calc} = 1.662 g/cm^3, μ(Mo Kα) = 50.45 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.

10 a) G. I. Nikonov, L. G. Kuzmina, S. F. Vyboishchikov, D. A. Lemenovskii, and J. A. K. Howard, *Chem. Eur. J.*, **5**, 2947 (1999). b) S. B. Duckett, L. G. Kuzmina, and G. I. Nikonov, *Inorg. Chem. Commun.*, **3**, 126 (2000).

11 Bond lengths for complexes of the type $Cp^{(*)}(CO)_2(L)WSiR_3$: see ref 2.

12 D. A. Straus, C. Zhang, G. E. Quimbita, S. D. Grumbine, R. H. Heyn, T. D. Tilley, A. L. Rheingold, and S. J. Geib, *J. Am. Chem. Soc.*, **112**, 2673 (1990).