

# Synthesis and structure of a tungsten dichlorosilyl dihydride complex

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## Abstract

The reaction of the donor-stabilized silylene complex *cis*-Cp<sup>\*</sup>(CO)<sub>2</sub>(H)W=SiHPh · THF (**3**, Cp<sup>\*</sup> = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) with LiAlH<sub>4</sub> followed by the protonation of the resulting Li[Cp<sup>\*</sup>(CO)<sub>2</sub>W(H)(SiH<sub>2</sub>Ph)] (**4**) with excess CF<sub>3</sub>COOH afforded the trihydride complex Cp<sup>\*</sup>(CO)<sub>2</sub>WH<sub>3</sub> (**6**). The structure of **6** was characterized using variable-temperature NMR studies and X-ray crystal analysis. Deprotonation of **6** with KH gave the anionic dihydride complex K[Cp<sup>\*</sup>(CO)<sub>2</sub>WH<sub>2</sub>] (**7**), which was converted into the dichlorosilyl dihydride complex Cp<sup>\*</sup>(CO)<sub>2</sub>W(H)<sub>2</sub>(SiHCl<sub>2</sub>) (**8**) on treatment with trichlorosilane. The X-ray crystal analysis of **8** revealed that it adopts a distorted pseudo-octahedral structure with a short W–Si bond, long Si–Cl bonds, and short contacts between the hydrides and silicon atom. Along with these structural features, the conformation of the silyl ligand around the W–Si bond may suggest the presence of a double interligand hypervalent interaction between the dichlorosilyl and hydrides ligands.

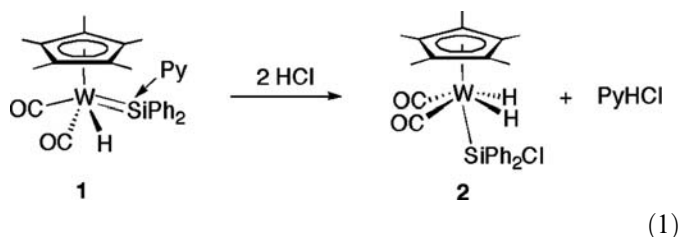
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**Keywords:** Tungsten; Silicon; Hydrides; Interligand hypervalent interaction; X-ray crystallography

## 1. Introduction

Polyhydride [1] and silyl-polyhydride [1,2] complexes of transition metals have attracted much attention because of their attractive structural features, such as classical or non-classical formulation and high fluxionality. Recently, we reported the addition of HCl to the donor-stabilized silylene complex *cis*-Cp<sup>\*</sup>(CO)<sub>2</sub>(H)W=SiPh<sub>2</sub> · Py (**1**) to give the chlorodiphenylsilyl dihydride complex Cp<sup>\*</sup>(CO)<sub>2</sub>W(H)<sub>2</sub>(SiPh<sub>2</sub>Cl) (**2**) (Eq. (1)), which had an interesting conformation around the W–Si bond, i.e., the Si–Cl bond occupied a position anti to one of the two W–H bonds [3]. Although this conformation suggested the possibility of an interligand hypervalent interaction (IHI) WH···SiCl [4] between the WH bonding orbital and Si–Cl antibonding orbital, the typical structural features of IHI for a monochlorosilyl hydride complex were not observed [3]. More recently, Nikonov suggested a possibility that conjugation between the π-system of phenyl groups and the Si–Cl σ\* orbital

diminishes the IHI in the studies of Cp(ArN)Nb-(PMe<sub>3</sub>)(H)(SiPh<sub>2</sub>Cl) and related complexes [5]. This suggestion prompted us to synthesize dihydride non-phenyl-substituted silyl complexes.



A versatile synthetic method for transition-metal silyl complexes is the silylation of anionic complexes with chlorosilanes, and the anionic complexes are often prepared by the deprotonation of hydride complexes. In the course of the reactivity studies of donor-stabilized silylene complexes of the type *cis*-Cp<sup>\*</sup>(CO)<sub>2</sub>(H)W=SiR<sub>2</sub> · Do, we obtained the trihydride complex Cp<sup>\*</sup>(CO)<sub>2</sub>WH<sub>3</sub> (**6**) by reacting *cis*-Cp<sup>\*</sup>(CO)<sub>2</sub>(H)W=SiHPh · THF (**3**) with LiAlH<sub>4</sub> to give Li[Cp<sup>\*</sup>(CO)<sub>2</sub>W(H)(SiH<sub>2</sub>Ph)] (**4**) followed by protonation with excess CF<sub>3</sub>COOH. To use trihydride complex **6** to

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synthesize tungsten dihydride silyl complexes, we studied the deprotonation of **6** and the silylation of the resulting anionic dihydride complex. The reaction of **6** with KH afforded the expected  $K[\text{Cp}^*(\text{CO})_2\text{WH}_2]$  (**7**), and the non-phenyl-substituted dichlorosilyl complex  $\text{Cp}^*(\text{CO})_2\text{W}(\text{H})_2(\text{SiHCl}_2)$  (**8**) was obtained by the reaction of **7** with trichlorosilane. In this paper, we describe the synthesis and structural characterization of these tungsten complexes **6**, **7**, and **8**.

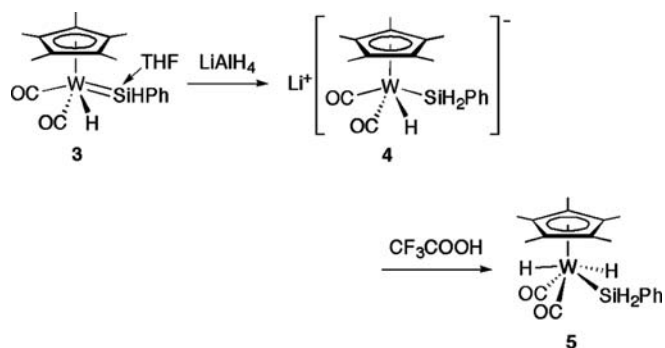
## 2. Results and discussion

### 2.1. Synthesis and characterization of $\text{Cp}^*(\text{CO})_2\text{WH}_3$

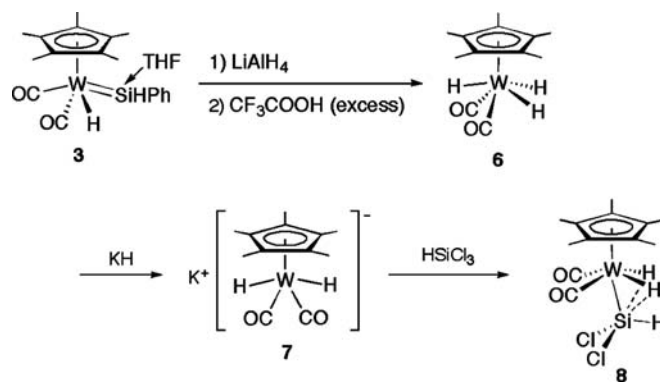
Recently, we synthesized  $\text{Cp}^*(\text{CO})_2\text{W}(\text{H})_2(\text{SiH}_2\text{Ph})$  (**5**) by reacting *cis*- $\text{Cp}^*(\text{CO})_2(\text{H})\text{W}=\text{SiHPh} \cdot \text{THF}$  (**3**) with  $\text{LiAlH}_4$  and protonating the resulting  $\text{Li}[\text{Cp}^*(\text{CO})_2\text{W}(\text{H})(\text{SiH}_2\text{Ph})]$  (**4**) with 1 equiv. of  $\text{CF}_3\text{COOH}$  (Scheme 1) [6]. The X-ray analysis of **5** revealed a rare pseudo-trigonal-prismatic structure for the  $\text{CpML}_5$ -type complex.

When **4** was treated with excess  $\text{CF}_3\text{COOH}$ , the desilylated product  $\text{Cp}^*(\text{CO})_2\text{WH}_3$  (**6**) was formed. For the convenient synthesis of **6**, the one-pot reaction of **3** with  $\text{LiAlH}_4$  in  $\text{Et}_2\text{O}$  followed by protonation with excess  $\text{CF}_3\text{COOH}$  (5.5 equiv.) was carried out to afford **6** in 80% yield (Scheme 2). X-ray analysis of **6** showed that the crystals contained three crystallographically independent molecules in the unit cell. Although the hydrides were not located, they have similar partial structures of the  $\text{Cp}^*\text{W}(\text{CO})_2$  moiety. The ORTEP drawing of one of them is shown in Fig. 1, and the bond angles, including the centroid of the  $\text{Cp}^*$  ligand and two carbonyl carbon atoms, are shown together with the corresponding angles for **5** in Table 1. The bond angles for **6** are very similar to the corresponding angles for **5**, suggesting the pseudo-trigonal-prismatic structure for **6**.

The room temperature  $^1\text{H}$  NMR spectrum of **6** in  $\text{THF}-d_8$  showed a sharp singlet at  $\delta -4.15$  (3H,  $J_{\text{WH}} = 48.9$  Hz) due to the hydrides, in addition to a  $\text{Cp}^*$  signal at  $\delta 2.27$ . The hydride region of the variable-temperature spectra of **6** is shown in Fig. 2. Decreasing the temperature to  $-114$  °C led to clear decoalescence into an  $\text{AB}_2$  type signal:  $\delta -3.72$  (1H, t,  $J_{\text{HH}} = 11.6$  Hz,  $J_{\text{WH}} = 49.7$  Hz) and



Scheme 1.



Scheme 2.

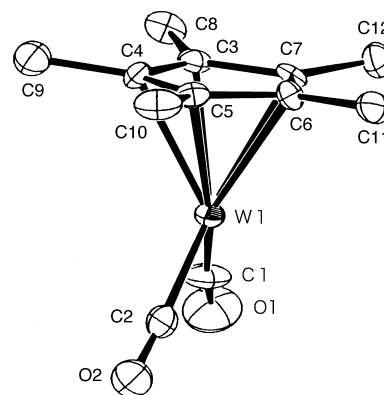


Fig. 1. ORTEP drawing of  $\text{Cp}^*(\text{CO})_2\text{WH}_3$  (**6**). Selected bond lengths (Å): W–C(1) 1.960(13), W–C(2) 2.004(15), C(1)–O(1) 1.160(18), C(2)–O(2) 1.105(19).

Table 1  
Bond angles (°) for **5** and **6**

	<b>5</b>	<b>6</b>		
		Molecule 1	Molecule 2	Molecule 3
C(1)–W–C(2) <sup>a</sup>	97.3(2)	96.4(5)	95.3(4)	95.0(5)
Cnt <sup>b</sup> –W–C(1) <sup>a</sup>	127.6(2)	129.8(5)	129.6(4)	129.7(5)
Cnt <sup>b</sup> –W–C(2) <sup>a</sup>	130.8(2)	131.9(4)	134.5(4)	135.2(4)

<sup>a</sup> C(1) and C(2) are the carbonyl carbon atoms.

<sup>b</sup> Cnt is the centroid of the  $\text{Cp}^*$  ring.

$-4.56$  (2H, d,  $J_{\text{HH}} = 11.6$  Hz,  $J_{\text{WH}} = 47.0$  Hz), whose  $T_1$  values (400 MHz) were 0.68 and 0.36 s, respectively. NOE experiments in which the  $\text{Cp}^*$  signal was irradiated at  $-114$  °C increased the intensity of the triplet (3.2%) and doublet (1.8%). These observations suggest that **6** is a trihydride complex with a pseudo-trigonal-prismatic structure.

In relation to **6**, it has been reported that *cis* and *trans* isomers of hydride dihydrogen complexes  $\text{Cp}^{(*)}(\text{CO})_2\text{W}(\text{H})_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ,  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) are formed by the photolysis of  $\text{Cp}^{(*)}(\text{CO})_3\text{WH}$  in  $\text{H}_2$ -containing matrices [7]. The structure of **6** suggested by our data corresponds to the *trans* structure, and the trihydride formulation seems more appropriate for the isolated  $\text{Cp}^*$  complex rather than the hydride dihydrogen formulation. To our

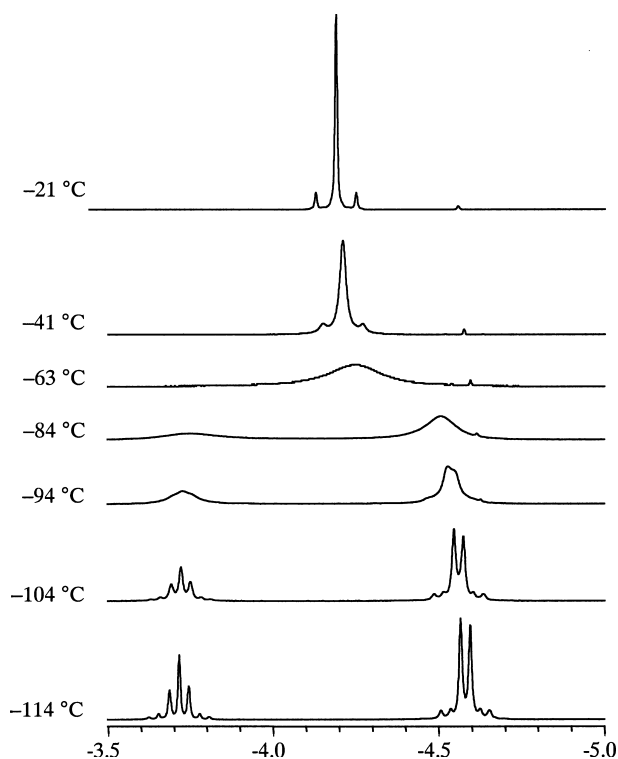


Fig. 2. Variable-temperature  $^1\text{H}$  NMR spectra of  $\text{Cp}^*(\text{CO})_2\text{WH}_3$  (**6**) showing the hydride region (400 MHz,  $\text{THF-}d_8$ ).

knowledge, the only previous example of a trihydride complex of the type  $\text{CpL}_2\text{MH}_3$  ( $\text{M}$  = group 6 metals) having a pseudo-trigonal-prismatic structure is  $\text{Cp}^*(\text{dppe})\text{MoH}_3$ , which is also highly fluxional in solution [8]. A pseudo-Bailar twist mechanism has been proposed for the dynamic processes.

## 2.2. Synthesis and characterization of $\text{K}[\text{Cp}^*(\text{CO})_2\text{WH}_2]$

To use **6** to synthesize new silyl dihydride complexes, its conversion into an anionic dihydride complex was examined. The reaction of **6** with  $\text{KH}$  in THF cleanly afforded the expected dihydride complex  $\text{K}[\text{Cp}^*(\text{CO})_2\text{WH}_2]$  (**7**) in 91% yield (Scheme 2). The  $^1\text{H}$  NMR spectrum of **7** in  $\text{THF-}d_8$  showed two sets of  $\text{Cp}^*$  and  $\text{WH}$  signals:  $\delta$  2.12 and  $-7.57$  ( $J_{\text{WH}} = 74.7$  Hz) for the *trans* isomer and  $\delta$  2.14 and  $-7.21$  ( $J_{\text{WH}} = 75.2$  Hz) for the *cis* isomer in a ratio of 63:37. These structural characterizations are based on their  $T_1$  values: 2.8 s at  $-110$  °C for the *trans* isomer and 0.59 s (minimum) at  $-80$  °C for the *cis* isomer. Although the value for the former did not reach a minimum value, the considerably larger value supports the *trans* configuration. In the IR spectrum of **7** in THF, two major  $\nu_{\text{CO}}$  absorption bands are observed at 1862 and 1752  $\text{cm}^{-1}$ . The average value of these bands is red shifted by 166  $\text{cm}^{-1}$  compared to that of the corresponding bands (2008 and 1938  $\text{cm}^{-1}$  in hexane) of the isoelectronic and isostructural dihydride complex  $\text{Cp}^*(\text{CO})_2\text{ReH}_2$  [9], supporting the anionic character of **7**.

## 2.3. Synthesis and structure of $\text{Cp}^*(\text{CO})_2\text{W}(\text{H})_2(\text{SiHCl}_2)$

The reaction of **7** with  $\text{HSiCl}_3$  in THF gave the silylated product  $\text{Cp}^*(\text{CO})_2\text{W}(\text{H})_2(\text{SiHCl}_2)$  (**8**) in 64% yield (Scheme 2). The molecular structure of **8** was determined by X-ray crystal analysis. The ORTEP drawing and selected bonding parameters are shown in Fig. 3. The drawing demonstrates that **8** adopts a distorted pseudo-octahedral structure with the  $\text{Cp}^*$  ligand occupying one coordination site. This type of structure has been found in **2** [3], and the  $\text{W-Si}$  bond length (2.4902(9) Å) in **8** is significantly shorter than that (2.5604(9) Å) in **2**. Similar very short  $\text{W-Si}$  bond (2.469(2) Å) has been observed in *trans*- $\text{Cp}^*(\text{CO})_2\text{W}(\text{P-Me}_3)(\text{SiCl}_2\text{SiCl}_3)$  (**9**) [10], comparing with the  $\text{W-Si}$  bond lengths (2.533–2.633 Å) in the corresponding non-chloro-substituted silyl complexes *trans*- $\text{Cp}^*(\text{CO})_2\text{W}(\text{PR}_3)(\text{SiR}_3)$  [11]. Interestingly, the  $\text{Si-Cl}$  bond lengths ( $\text{Si-Cl}(1) = 2.0981(14)$ ,  $\text{Si-Cl}(2) = 2.1084(13)$  Å) in **8** are also very similar to the  $\text{Si}_\alpha\text{-Cl}$  bond lengths (2.101(3), 2.108(3) Å) in **9**. The  $\text{Si}_\alpha\text{-Cl}$  bond lengths are considerably longer than the  $\text{Si}_\beta\text{-Cl}$  bond lengths (2.027(3)–2.034(3) Å), which are comparable to the  $\text{Si-Cl}$  bond lengths in chlorosilanes [10]. These structural characteristics, the short  $\text{M-Si}$  and elongated  $\text{Si-Cl}$  bonds, observed in **9** and related ruthenium chloro-substituted silyl complexes [12] have been attributed to  $\pi$ -back bonding between the metal center and  $\text{Si-Cl}$  antibonding orbitals.

Another characteristic feature of the structure of **8** is short contacts between the silicon atom and two hydrides:  $\text{Si}\cdots\text{H}(1) = 1.91(3)$  and  $\text{Si}\cdots\text{H}(2) = 1.90(3)$  Å, suggesting  $\text{Si}\cdots\text{H}$  interactions, although the low accuracy of the hydride positions determined in the X-ray analyses must be considered. In addition, considering the interesting conformation around the  $\text{W-Si}$  bond, where each chlorine

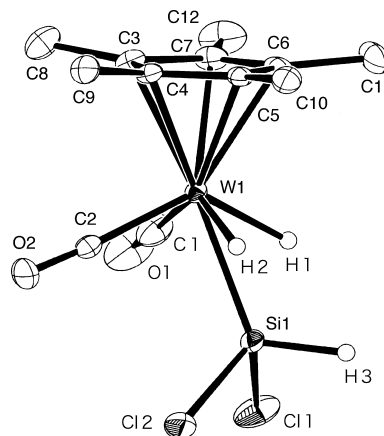


Fig. 3. ORTEP drawing of  $\text{Cp}^*(\text{CO})_2\text{W}(\text{H})_2(\text{SiHCl}_2)$  (**8**). Selected bond lengths (Å) and angles (°):  $\text{W-Si}$  2.4902(9),  $\text{W-C}(1)$  2.002(4),  $\text{W-C}(2)$  1.995(3),  $\text{W-H}(1)$  1.67(4),  $\text{W-H}(2)$  1.63(3),  $\text{Si-Cl}(1)$  2.0981(14),  $\text{Si-Cl}(2)$  2.1084(13),  $\text{C}(1)\text{-O}(1)$  1.139(5),  $\text{C}(2)\text{-O}(2)$  1.135(4),  $\text{H}(1)\cdots\text{H}(2)$  2.05(5);  $\text{Si-W-C}(1)$  83.67(12),  $\text{Si-W-C}(2)$  82.91(11),  $\text{Si-W-H}(1)$  50.2(12),  $\text{Si-W-H}(2)$  49.6(12),  $\text{C}(1)\text{-W-C}(2)$  85.41(17),  $\text{C}(1)\text{-W-H}(1)$  77.9(13),  $\text{C}(2)\text{-W-H}(2)$  82.1(12),  $\text{H}(1)\text{-W-H}(2)$  76.8(18),  $\text{W-Si-Cl}(1)$  116.62(5),  $\text{W-Si-Cl}(2)$  115.28(4),  $\text{Cl}(1)\text{-Si-Cl}(2)$  100.36(5).

atom occupies a position anti to one of the hydrides (torsion angles: H(1)–W–Si–Cl(2) = 180(1), H(2)–W–Si–Cl(1) = 178(1°), the W–Si bond shortening and Si–Cl bond lengthening in **8** may be attributable to a double interligand hypervalent interaction  $\text{WH}_2 \cdots \text{SiCl}_2$ . Recently, the possibility of this type of interaction was suggested for  $\text{Cp}^*(\text{R}_3\text{P})\text{Ru}(\text{H})_2(\text{SiCl}_2\text{R})$  by Nikonov [4h], who pointed out a close analogy between the participation of two Si–Cl antibonding orbitals of the  $\text{SiCl}_2\text{R}$  fragment in the double IHI in  $\text{Cp}^*(\text{R}_3\text{P})\text{Ru}(\text{H})_2(\text{SiCl}_2\text{R})$  [4h] and that in the  $\pi$ -back-bonding interaction in  $\text{Cp}(\text{R}_3\text{P})_2\text{Ru}(\text{SiCl}_2\text{R})$  [12], although the electron-donating counterparts are different, i.e., electrons in the Ru–H bond orbitals in the former and a metal centered lone pair in the latter. In these complexes, short Ru–Si and long Si–Cl bonds are observed: for example, Ru–Si = 2.2950(5) Å and Si–Cl = 2.1170(7), 2.1271(7) Å for  $\text{Cp}^*(i\text{Pr}_3\text{P})\text{Ru}(\text{H})_2(\text{SiCl}_2\text{Me})$  [4h] and Ru–Si = 2.294(2) Å and Si–Cl = 2.145(3), 2.153(3) Å for  $\text{Cp}(\text{Me}_3\text{P})_2\text{Ru}(\text{SiCl}_2\text{Me})$  [12]. Similar structural characteristics are found for the W–Si and Si–Cl bonds in **8** and **9** as described above and may reflect the participation of the Si–Cl antibonding orbitals in their interactions, the double IHI in **8** and the  $\pi$ -back-bonding interaction in **9**. Compared to the Si–Cl bonds in the ruthenium complexes, the Si–Cl bonds in **8** and **9** are relatively short. This is probably due to the presence of carbonyl ligands, which would reduce the electron density on the metal and the basicity of the hydrides to decrease relatively both types of interactions with the Si–Cl antibonding orbitals. Thus, we have synthesized and characterized new dichlorosilyl dihydride complex **8**, whose structural characteristics may be ascribed to the double IHI between the dichlorosilyl and hydrides ligands. Further studies of the reactivity of **8** are in progress.

### 3. Experimental

#### 3.1. General comments

All reactions and procedures were carried out under an atmosphere of nitrogen using standard glovebox, Schlenk, and high-vacuum-line techniques.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra were recorded on a JEOL JNM-GSX400 spectrometer. The temperature of the NMR probe was calibrated with methanol. The conventional inversion-recovery method (180- $\tau$ -90) was used to determine the relaxation times  $T_1$ . IR spectra were obtained on a Shimadzu FTIR-8100M spectrometer. Elemental analyses were performed on a Yanaco CHN Corder MT-6.

Diethyl ether, hexane, pentane, tetrahydrofuran, toluene, tetrahydrofuran- $d_8$ , and toluene- $d_8$  were distilled from sodium benzophenone ketyl. Acetonitrile was distilled from calcium hydride. Trifluoroacetic acid (Aldrich) and trichlorosilane (Tokyo Kasei) were degassed and vacuum transferred immediately prior to use. Phenylsilane (Tokyo Kasei) was stored over 4 Å molecular sieves. Lithium aluminum hydride (1.0 M solution in diethyl ether, Aldrich)

was used as received. Potassium hydride obtained as 30% dispersion in mineral oil (Aldrich) was washed with hexane and stored as a powder in the glovebox. *cis*- $\text{Cp}^*(\text{CO})_2(\text{H})\text{W}=\text{SiHPh} \cdot \text{THF}$  (**3**) was prepared by the photolysis of  $\text{Cp}^*(\text{CO})_3\text{WMe}$  and  $\text{PhSiH}_3$  in THF [6].  $\text{Cp}^*(\text{CO})_3\text{WMe}$  was prepared according to the literature methods [13].

#### 3.2. Synthesis of $\text{Cp}^*(\text{CO})_2\text{WH}_3$ (**6**)

To a Schlenk flask containing *cis*- $\text{Cp}^*(\text{CO})_2(\text{H})\text{W}=\text{SiHPh} \cdot \text{THF}$  (**3**) (1.162 g, 2.10 mmol) at  $-196^\circ\text{C}$  was added diethyl ether (14 mL) by vacuum transfer. A solution of  $\text{LiAlH}_4$  in diethyl ether (1.0 M, 2.3 mL, 2.3 mmol) was added to the frozen mixture via syringe under nitrogen atmosphere. The mixture was thawed in an acetone bath ( $-60^\circ\text{C}$ ) and then allowed to warm to room temperature. After being stirred for 15 min, the mixture was cooled to  $-60^\circ\text{C}$ , and methanol (0.9 mL) was added to destroy unreacted  $\text{LiAlH}_4$ . Trifluoroacetic acid (0.9 mL) was vacuum transferred to the flask at  $-196^\circ\text{C}$ . The mixture was allowed to warm to room temperature and stirred for 15 min. After removal of the solvent, the residue was extracted with hexane ( $5 \times 4$  mL), and the extract was filtered through glass fiber filter paper. Removal of the solvent left a yellowish solid, which was recrystallized from pentane (1.5 mL) to give **6** (633 mg, 1.67 mmol, 80%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_5\text{CD}_3$ , r.t.)  $\delta$   $-3.90$  (s,  $^1J_{\text{WH}} = 48.9$  Hz, 3H, WH), 1.88 (s, 15H, Cp\*);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_5\text{CD}_3$ , r.t.)  $\delta$  11.8 ( $\text{C}_5\text{Me}_5$ ), 103.9 ( $\text{C}_5\text{Me}_5$ ), 208.4 (CO,  $^1J_{\text{WC}} = 123.4$  Hz); IR (toluene)  $\nu_{\text{CO}} = 1989$  (s), 1918 (s)  $\text{cm}^{-1}$ ; Anal. Calc. for  $\text{C}_{12}\text{H}_{18}\text{O}_2\text{W}$ : C, 38.12; H, 4.80. Found: C, 38.39; H, 4.67%.

#### 3.3. Synthesis of $\text{K}[\text{Cp}^*(\text{CO})_2\text{WH}_2]$ (**7**)

To a reaction vessel containing  $\text{Cp}^*(\text{CO})_2\text{WH}_3$  (**6**) (602 mg, 1.59 mmol) and potassium hydride (70 mg, 1.75 mmol) at  $-196^\circ\text{C}$  was added THF (11 mL) by vacuum transfer. The mixture was allowed to warm to room temperature and stirred for 1.5 h. After removal of the solvent, acetonitrile (4 mL) was added to the residue, and the mixture was filtered through a glass filter. The solvent was removed in vacuo, and the residual solid was washed with diethyl ether (2 mL) to give **7** (600 mg, 1.44 mmol, 91%) as a yellow solid.  $^1\text{H}$  NMR ( $\text{C}_4\text{D}_8\text{O}$ , r.t.)  $\delta$   $-7.57$  (s,  $^1J_{\text{WH}} = 74.7$  Hz, 2H, WH (*trans*-**7**)),  $-7.21$  (s,  $^1J_{\text{WH}} = 75.2$  Hz, 2H, WH (*cis*-**7**)), 2.12 (s, 15H, Cp\* (*trans*-**7**)), 2.14 (s, 15H, Cp\* (*cis*-**7**));  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_4\text{D}_8\text{O}$ , r.t.)  $\delta$  12.9 ( $\text{C}_5\text{Me}_5$  (*cis*-**7**)), 13.2 ( $\text{C}_5\text{Me}_5$  (*trans*-**7**)), 97.7 ( $\text{C}_5\text{Me}_5$  (*trans*-**7**)), 99.8 ( $\text{C}_5\text{Me}_5$  (*cis*-**7**)), 242.9 ( $^1J_{\text{WC}} = 154.8$  Hz, CO (*trans*-**7**)), 250.3 ( $^1J_{\text{WC}} = 154.8$  Hz, CO (*cis*-**7**)); IR (THF)  $\nu_{\text{CO}} = 1862$  (s), 1752 (s)  $\text{cm}^{-1}$ .

#### 3.4. Synthesis of $\text{Cp}^*(\text{CO})_2\text{W}(\text{H})_2(\text{SiHCl}_2)$ (**8**)

To a reaction vessel containing  $\text{K}[\text{Cp}^*(\text{CO})_2\text{WH}_2]$  (**7**) (807 mg, 1.94 mmol) at  $-196^\circ\text{C}$  was added THF (20 mL)

and  $\text{HSiCl}_3$  (1.0 mL) by vacuum transfer. The mixture was stirred for 5 min at  $-60^\circ\text{C}$  and then stirred for 50 min at room temperature. After removal of the solvent in vacuo, the residue was extracted with diethyl ether ( $5 \times 5$  mL). The extract was filtered through glass fiber filter paper. After the solution was concentrated to ca. 1 mL, pentane (6 mL) was added to give an orange solid. The mixture was cooled to  $-60^\circ\text{C}$  and the supernatant was decanted to leave **8** (588 mg, 1.23 mmol, 64%) as an orange solid.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_5\text{CD}_3$ ,  $-60^\circ\text{C}$ )  $\delta$  -6.34 (d,  $^3J_{\text{HH}} = 7.5$  Hz,  $^1J_{\text{WH}} = 55.3$  Hz, 2H, WH), 1.52 (s, 15H,  $\text{Cp}^*$ ), 8.11 (t,  $^3J_{\text{HH}} = 7.5$  Hz,  $^1J_{\text{SiH}} = 286.9$  Hz,  $^2J_{\text{WH}} = 23.6$  Hz, 1H, SiH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_5\text{CD}_3$ ,  $-60^\circ\text{C}$ )  $\delta$  10.6 ( $\text{C}_5\text{Me}_5$ ), 101.3 ( $\text{C}_5\text{Me}_5$ ), 217.7 (CO,  $^1J_{\text{WC}} = 146$  Hz);  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_5\text{CD}_3$ ,  $-60^\circ\text{C}$ )  $\delta$  10.3; IR (toluene)  $\nu_{\text{CO}} = 2026$  (s), 1966 (s)  $\text{cm}^{-1}$ ; Anal. Calc. for  $\text{C}_{12}\text{H}_{18}\text{Cl}_2\text{O}_2\text{SiW}$ : C, 30.21; H, 3.80. Found: C, 30.63; H, 3.98%.

### 3.5. X-ray crystal structure determination

Single crystals of **6** and **8** were obtained by sublimation at  $50^\circ\text{C}$  and recrystallization from toluene/hexane, respectively. All measurements were made on a Rigaku Mercury CCD area detector with graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71070$  Å). The data were corrected for Lorentz and polarization effects. The structures were solved by direct method (SIR92) [14] and expanded using difference Fourier techniques (DIRDIF99) [15]. The refinement was carried out using full-matrix least-squares method on  $F^2$ . All non-hydrogen atoms were refined anisotropi-

cally, and the hydrogen atoms of the  $\text{Cp}^*$  ligands were calculated and refined with a riding model. At this stage, in **6**, all of three tungsten hydrides in each independent molecule could not be found in geometrically reasonable positions, and therefore no further consideration was made for the hydrides. On the other hand, in **8**, two tungsten hydrides and one silicon hydride were clearly located in the difference map, and the formers were refined isotropically and the latter refined with a riding model. Atomic scattering factors were taken from International Tables for X-ray Crystallography [16]. All calculations were performed using the CrystalStructure crystallographic software package [17]. Details of crystallographic analyses are summarized in Table 2.

### 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC 298786 for complex **6** and CCDC 298787 for complex **8**. Copies of this information may be obtained free of charge from the Director, CCDC 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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### References

Table 2  
Crystallographic data for **6** and **8**

	<b>6</b>	<b>8</b>
Formula	$\text{C}_{12}\text{H}_{18}\text{O}_2\text{W}$	$\text{C}_{12}\text{H}_{18}\text{Cl}_2\text{O}_2\text{SiW}$
Formula weight	378.12	477.11
Crystal size (mm)	$0.20 \times 0.10 \times 0.10$	$0.20 \times 0.15 \times 0.15$
Color of crystals	Yellow	Yellow
Temperature ( $^\circ\text{C}$ )	-100	-100
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)	$Pbca$ (No. 61)
$a$ (Å)	19.522(5)	13.295(3)
$b$ (Å)	8.089(2)	16.062(4)
$c$ (Å)	24.814(6)	15.197(4)
$V$ (Å <sup>3</sup> )	3918.5(17)	3245.4(13)
$Z$	12	8
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.923	1.953
$\mu$ (Mo $\text{K}\alpha$ ) ( $\text{cm}^{-1}$ )	88.344	75.211
$2\theta_{\text{max}}$ ( $^\circ$ )	55.0	55.0
Number of reflections measured	32026	28287
Number of independent reflections ( $R_{\text{int}}$ )	8841 (0.045)	3687 (0.027)
Number of parameters	452	190
$R_1$ ( $I > 2.00\sigma(I)$ )	0.0448	0.0218
$R$ (all data)	0.0687	0.0329
$wR_2$ (all data)	0.1064	0.0472
GOF	1.012	1.097

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}}$$

- [1] G.J. Kubas, Metal Dihydrogen and  $\sigma$ -Bond Complexes, Kluwer Academic/Plenum Publishers, New York, 2001.
- [2] (a) U. Schubert, Adv. Organomet. Chem. 30 (1990) 151; (b) J.Y. Corey, J. Braddock-Wilking, Chem. Rev. 99 (1999) 175.
- [3] H. Sakaba, T. Hirata, C. Kabuto, H. Horino, Chem. Lett. (2001) 1078.
- [4] (a) For example G.I. Nikonov, L.G. Kuzmina, S.F. Vyboishchikov, D.A. Lemenovskii, J.A.K. Howard, Chem. Eur. J. 5 (1999) 2947; (b) V.I. Bakhmutov, J.A.K. Howard, D.A. Keen, L.G. Kuzmina, M.A. Leech, G.I. Nikonov, E.V. Vorontsov, C.C. Wilson, J. Chem. Soc., Dalton Trans. (2000) 1631; (c) G.I. Nikonov, P. Mountford, S.K. Ignatov, J.C. Green, M.A. Leech, L.G. Kuzmina, A.G. Razuvaev, N.H. Rees, A.J. Blake, J.A.K. Howard, D.A. Lemenovskii, J. Chem. Soc., Dalton Trans. (2001) 2903; (d) G.I. Nikonov, L.G. Kuzmina, J.A.K. Howard, J. Chem. Soc., Dalton Trans. (2002) 3037; (e) S.R. Dubberley, S.K. Ignatov, N.H. Rees, A.G. Razuvaev, P. Mountford, G.I. Nikonov, J. Am. Chem. Soc. 125 (2003) 644; (f) K.Yu. Dorogov, E. Dumont, N.-N. Ho, A.V. Churakov, L.G. Kuzmina, J.-M. Poblet, A.J. Schultz, J.A.K. Howard, R. Bau, A. Lledos, G.I. Nikonov, Organometallics 23 (2004) 2845; (g) S.K. Ignatov, N.H. Rees, B.R. Tyrrell, S.R. Dubberley, A.G. Razuvaev, P. Mountford, G.I. Nikonov, Chem. Eur. J. 10 (2004) 4991; (h) A.L. Osipov, S.M. Gerdov, L.G. Kuzmina, J.A.K. Howard, G.I. Nikonov, Organometallics 24 (2005) 587.

- [5] G.I. Nikonov, P. Mountford, S.R. Dubberley, *Inorg. Chem.* 42 (2003) 258.
- [6] H. Sakaba, T. Hirata, C. Kabuto, K. Kabuto, *Organometallics* (in press).
- [7] R.L. Sweany, *J. Am. Chem. Soc.* 108 (1986) 6986.
- [8] (a) J.C. Fettinger, B.A. Pleune, R. Poli, *J. Am. Chem. Soc.* 118 (1996) 4906;  
(b) B. Pleune, R. Poli, J.C. Fettinger, *Organometallics* 16 (1997) 1581;  
(c) F. Abugideiri, J.C. Fettinger, B. Pleune, R. Poli, C.A. Bayse, M.B. Hall, *Organometallics* 16 (1997) 1179.
- [9] R.G. Ball, A.K. Campen, W.A.G. Graham, P.A. Hamley, S.G. Kazarian, M.A. Ollino, M. Poliakoff, A.J. Rest, L. Sturgeooff, I. Whitewell, *Inorg. Chim. Acta* 259 (1997) 137.
- [10] W. Malisch, R. Lankat, W. Seelbach, J. Reising, M. Noltemeyer, R. Pikel, U. Posset, W. Kiefer, *Chem. Ber.* 128 (1995) 1109.
- [11] (a) S. Sharma, R.N. Kapoor, F. Cervantes-Lee, K.H. Pannell, *Polyhedron* 10 (1991) 1177;  
(b) S. Schmitzer, U. Weis, H. Kab, W. Buchner, W. Malisch, T. Polzer, U. Posset, W. Kiefer, *Inorg. Chem.* 32 (1993) 303;  
(c) W. Malisch, S. Schmitzer, R. Lankat, M. Neumayer, F. Prechtel, W. Adam, *Chem. Ber.* 128 (1995) 1251.
- [12] S.T.N. Freeman, J.L. Petersen, F.R. Lemke, *Organometallics* 23 (2004) 1153, and references therein.
- [13] K.A. Mahmoud, A.J. Rest, H.G. Alt, M.E. Eichner, B.M. Jansen, *J. Chem. Soc., Dalton Trans.* (1984) 175.
- [14] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.* 27 (1994) 435.
- [15] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.
- [16] D.T. Cromer, J.T. Waber, *International Tables for X-ray Crystallography*, vol. 4, Kynoch Press, Birmingham, England, 1974.
- [17] *CrystalStructure 3.7*, Crystal Structure Analysis Package, Rigaku and Rigaku/MSC, 2000–2005.