# Isolation of a Hydrogen-Bridged Bis(silylene) Tungsten Complex: A Snapshot of a Transition State for 1,3-Hydrogen Migration

Hisako Hashimoto,[*,†] Yuto Odagiri,[†] Yasuhiro Yamada,[†] Nozomi Takagi,[‡] Shigeyoshi Sakaki,[‡] and Hiromi Tobita[*,†]

[†]Departmet of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
[‡]Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 603-8103, Japan

Ⓢ Supporting Information

**ABSTRACT:** A hydrogen-bridged bis(silylene) complex, which can be viewed as a snapshot of a transition state for 1,3-hydrogen migration, was isolated, and its unprecedented $WSi_2H$ four-membered-ring structure with a short diagonal Si−Si distance was revealed by X-ray crystallography. NMR studies including determination of the W−Si, Si−Si, and Si−H coupling constants and theoretical calculations suggest that a novel multicenter bond is formed in the $WSi_2H$ system, in which the bridging hydrogen takes on a hydridic nature.

Although participation of four-centered transition states is often presumed in the important reactions involving metal-mediated cleavage/formation of chemical bonds such as olefin metathesis[1] and σ-bond metathesis,[2] it is generally very difficult to get information on such species except through theoretical calculations. Four-centered transition states are also postulated to be involved in the 1,3-migration of R groups on silyl(silylene) complexes **A** (Chart 1).[3,4] Since this 1,3-

**Chart 1**
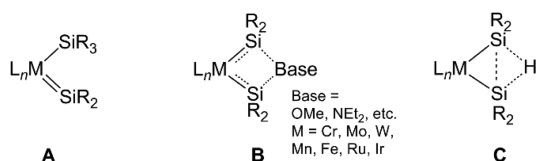


migration involves activation of usually robust Si−X σ-bonds (X = H, C, O, etc.), it is regarded as one of the fundamental processes for transformations of silicon compounds.

Our group[3] and Pannell's group[4] previously reported that 1,3-alkyl/aryl migration occurs extensively in the photochemical reactions of disilanyl iron complexes, leading to scrambling of substituents on silicon atoms. We proved afterward that this extremely facile 1,3-migration proceeds on silyl(silylene) complexes,[5] through the isolation of a silyl(silylene)iron complex and the direct observation of the occurrence of 1,3-group migration on it.[6] We have also isolated a number of base-stabilized bis(silylene) complexes **B** that can be viewed as a snapshot of transition states for the 1,3-migration of groups having lone pairs on them.[7,8] Here we report the isolation of the first hydrogen-bridged four-membered-ring complex **C** (Chart 1), which can be viewed

as a snapshot of a transition state for 1,3-hydrogen migration between two silicon atoms. Unprecedented structural features and bonding aspects of this complex were elucidated by X-ray diffraction study, multinuclear NMR studies, and theoretical calculations.

In a preliminary experiment, we observed that a hydrogen-bridged complex $Cp*W(CO)_2\{Me_2Si\cdots H\cdots SiH(t\text{-}Bu)\}$ (**1**) $(Cp* = \eta^5\text{-}C_5Me_5)$ was formed in $C_6D_6$ as a main product by the photochemical reaction of $Cp*W(CO)_3Me$ with a trihydrodisilane $H_3SiSiMe_2(t\text{-}Bu)$ (Scheme 1).[9] Thus, the [1]H

**Scheme 1**
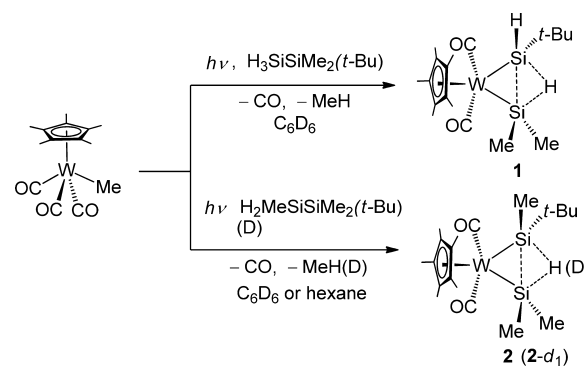


NMR spectrum of the reaction mixture (toluene-$d_8$, 230 K) exhibited two sets of doublet resonances (0.44, 1.01 ppm) for two inequivalent methyl groups, one doublet resonance (4.43 ppm) for a terminal SiH, and one multiplet resonance (2.69 ppm) assignable to a bridging SiHSi, in addition to two singlet resonances for t-Bu and Cp* groups (see Figure S1 in Supporting Information (SI)). The multiplet for the bridging hydrogen (2.69 ppm) was remarkably upfield-shifted compared with those for normal SiH protons (~3.5 ppm), implying that the hydrogen is strongly shielded by bonding to two electropositive silicon atoms. Furthermore, the [1]H−[1]H correlation spectroscopy (COSY) clearly showed that the multiplet resonance of SiHSi is correlated with both the two Me signals and the terminal SiH signal (Figure S2 in SI). These observations strongly support the hydrogen-bridged structure of **1**. The ^{29}Si {^{1}H decoupled} NMR spectrum (toluene-$d_8$, 250

K) exhibited resonances at 70.9 and 35.4 ppm with tungsten–silicon satellite couplings $^1J(^{183}W-^{29}Si)$ = 85.4 and 96.3 Hz, respectively. Although isolation of **1** was unsuccessful because of its extreme instability, by employing a dihydrodisilane $H_2MeSiSiMe_2(t\text{-Bu})$ as a starting material, we have succeeded in isolation of $Cp*W(CO)_2\{Me_2Si\cdots H\cdots SiMe(t\text{-Bu})\}$ (**2**) in 48% yield as yellow-brown crystals.[9] Complex **2** is air- and moisture-sensitive and gradually decomposes above 60 °C in solution, but is stable in the solid state. We also obtained a deuterated analog of **2** having one deuterium at the bridging position, $Cp*W(CO)_2\{Me_2Si\cdots D\cdots SiMe(t\text{-Bu})\}$ (**2-***d*), in 41% yield by the reaction with $D_2MeSiSiMe_2(t\text{-Bu})$.

The X-ray crystal structure analysis of **2** revealed its four-membered-ring structure having an almost planar $WSi_2H$ framework (Figure 1): The dihedral angle between the W1–
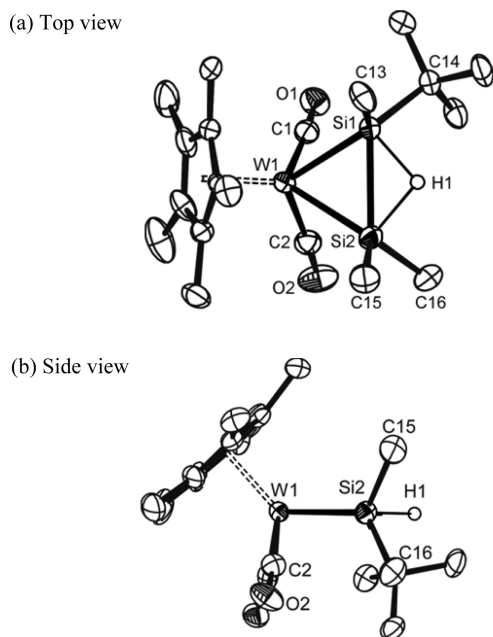


**Figure 1.** Molecular structure of **2**: (a) top view (b) side view. The thermal ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity except H1. Selected bond lengths (Å) and angles (deg): W1–Si1, 2.489(2); W1–Si2, 2.487(2); W1–C1, 1.942(9); W1–C2, 1.945(9); C1–O1, 1.179(11); C2–O2, 1.167(11); Si1⋯Si2, 2.455(3); Si1⋯H1, 1.71(8); Si2⋯H1, 1.75(9); Si1–W1–Si2, 59.11(8); W1–Si1–H1, 106(3); W1–Si2–H1, 105(3); Si1–H1–Si2, 90(4).

Si2–Si1 and Si2–Si1–H1 planes is 179(4)°. Both W–Si bonds (2.489(2) and 2.487(2) Å) are longer than the known W=Si double bonds (2.35–2.42 Å)[10] but are close to those of tungsten complexes of type **B** (2.49–2.50 Å).[11] The H1 atom bridges two Si atoms nearly symmetrically. The Si–H bonds (1.71(8) and 1.75(9) Å)[12] are about 17% longer than the typical Si–H single bond in tetrahedral silanes (1.48 Å) and comparable with those of M–Si–H three-center two-electron (3c-2e) bonds in $\eta^2$-Si–H transition metal complexes.[13] The most striking structural feature is the Si⋯Si distance (2.455(3) Å), which is within the known Si–Si single bond lengths (2.34–2.70 Å)[14] and significantly shorter than those of the type **B** complexes (2.56–2.72 Å),[8] which have no direct Si–Si bonds.[15] These structural features imply the existence of Si⋯H and Si⋯Si bonding interactions.

$^1H$, $^{13}C$, and $^{29}Si$ NMR, and IR spectral data of **2** are all consistent with the solid state structure. The $^1H$ NMR spectrum of **2** ($C_6D_6$ at 298 K) exhibits a resonance of SiHSi at 2.92 ppm as a pseudo-decet due to the coupling with the protons of inequivalent three methyl groups whose signals appear at 0.51, 0.57, and 0.93 ppm. The observation of this coupling with 9 protons confirms that the hydrogen is bridging two Si atoms rather than taking a terminal position. The upfield-shift of the resonance (2.92 ppm) for the bridging hydrogen atom resembles that of **1**. The $^{29}Si$ NMR spectrum ($C_6D_6$, 298 K) of **2** shows two resonances for $SiMe_2$ and $SiMe(t\text{-Bu})$ at 43.6 and 70.2 ppm with satellite couplings, $^1J(W-Si)$ = 86.5 and 94.8 Hz, respectively: The assignment was confirmed by $^1H$ -$^{29}Si$ COSY spectrum (Figure S4 in SI). Importantly, we were able to determine three coupling constants, $J(W-Si)$, $J(Si-H)$, and $J(Si-Si)$, which provide valuable information about the bonding aspects. In general, the spin–spin coupling constants reflect the s character of the nuclei involved in the bond. The tungsten–silicon coupling constants $J(W-Si)$ for **1** (85.4 and 96.3 Hz) and **2** (86.5 and 94.8 Hz) are nearly intermediate between those of silyl (sp$^3$ Si) and silylene ligands (sp$^2$ Si) in tungsten complexes, e.g., $J(W-Si)$ = 30.5 Hz for $WSiMe_3$ and 154.9 Hz for $W=SiMes_2$ in $Cp*W(CO)_2(SiMe_3)(=SiMes_2)$.[11] These values are close to those reported for tungsten complexes of type **B** (92–132 Hz).[12] In the case of **2**, the silicon–hydrogen coupling constant $J(Si-H)$ was estimated to be 23 Hz by the $^1H$ homodecoupling method.[16] This value is slightly larger than Schubert's criterion (20 Hz), which indicates the existence of weak Si–H bonding interaction.[13] In accord with this fact, a weak and broad Si–H stretching-vibration band was observed at 1288 cm$^{-1}$ in the IR spectrum, which is considerably low-wavenumber-shifted from the stretching vibration bands of normal Si–H σ-bonds (~2100 cm$^{-1}$). The corresponding Si–D stretching band of **2-***d* appeared at 951 cm$^{-1}$ in the theoretically expected region, which confirms the assignment. Furthermore, the Si–Si coupling constant $J(Si-Si)$ was determined to be 28.2 Hz by an INEPT-INADEQUATE $^{29}Si$ NMR measurement of **2**.[15,17] This value is substantially larger than those in 1,3-cyclo-disiloxanes (3.8–4.8 Hz) that have no direct Si–Si bond,[17] although it is far smaller than typical values in disilanes having a Si–Si single bond (80–90 Hz).[18] The value of 28.2 Hz is more than twice as large as the $J(Si-Si)$ value (13.2 Hz) for $Cp*W(CO)_2\{Me_2Si\cdots(OMe)\cdots SiMe(t\text{-Bu})\}$ (**3**), a type **B** complex of tungsten (vide infra).[19] These observations suggest that a significant bonding interaction is formed between two Si atoms in **2**.

In terms of electron count and valence bond description, the bonding in type **C** complexes such as **1** and **2** can be represented by a combination of two canonical forms in which a Si–H "σ-bonding electron pair" on the silyl ligand interacts with an empty p orbital of the silylene ligand (Chart 2). This could also be viewed as an agostic interaction of the Si–H bond with the silylene silicon center. This sort of coordination of a σ-bonding electron pair to a silylene ligand is unprecedented,

**Chart 2**
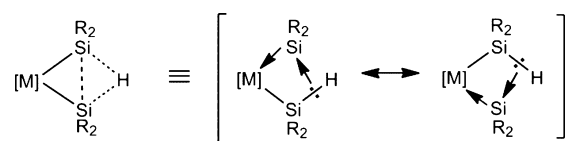
although there is an example of coordination of a π-bonding electron pair to a silylene ligand.[20] In this representation, the SiHSi moiety can be regarded as a 3-electron-donor ligand in a covalent model. Thus, the tungsten center satisfies the 18 electron rule, which is consistent with the stability of these complexes.

To understand this unusual bonding, we performed DFT calculations of **2** with the B3PW91 functional using the Gaussian 09 program.[9] Important bonding orbitals of the optimized structure, **2**-opt, are depicted in Figure 2.[21] The
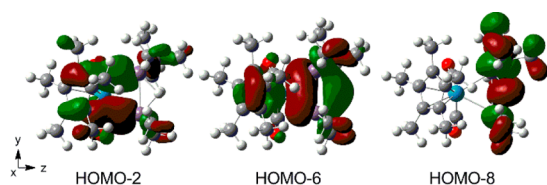


**Figure 2.** Important Kohn−Sham orbitals of **2**-opt.

HOMO-2 represents the W−Si σ-bonding interaction between the $d_{yz}$ orbital of the W center and two sets of $sp^2$-hybrid orbitals of two Si atoms. The HOMO-6 consists of the $d_{z^2}$ orbital of the W center, two sets of $sp^2$-hybrid orbitals of two Si atoms, and the 1s orbital of the bridging hydrogen atom. The HOMO-8 is mainly composed of two p-type orbitals of Si atoms and 1s orbital of the bridging hydrogen, which corresponds to a $Si_2H$ 3c-2e interaction (see also Figure S7 in SI). A unique combination of these three bonding orbitals results in a novel four-center bonding at the $WSi_2H$ moiety. Notably, the Si···Si and Si···H bonding interactions are involved in the HOMO-6 and HOMO-8. The Wiberg bond indices (WBIs) between two Si atoms in **2**-opt were calculated to be 0.35, which are roughly half of the calculated value for the Si−Si single bond of $Me_3Si−SiMe_3$ (0.92). Similarly, the WBI between the bridging hydrogen and each Si atom (0.42, 0.45) is about half of that (0.96) for the Si−H bond in $H_3Si−SiH_3$. These data indicate that the Si···Si and Si···H bonding interactions are weaker than the corresponding single bonds but are sufficiently significant to stabilize this peculiar four-membered-ring structure of **2**. In addition, calculated charge distribution indicates that the Si centers are highly electrophilic while the bridging hydrogen is hydridic: NBO charges of $q(Si1)$, $q(Si2)$, and $q(H1)$ are +1.45, +1.36, and −0.15, respectively (see Table S4 in SI).

As it can be expected from the charge distribution, complex **2** reacted with MeOH at room temperature with evolution of dihydrogen to give $Cp*W(CO)_2\{Me_2Si···(OMe)···SiMe(t-Bu)\}$ (**3**) in 71% isolated yield (Scheme 2). Complex **3** was characterized as the **B**-type complex based on its spectroscopic features: i.e., the downfield-shifted $^{29}Si$ NMR resonances (97.5 ppm for $SiMe_2$ and 111.4 ppm for SiMe(t-Bu)) and the upfield-

**Scheme 2**
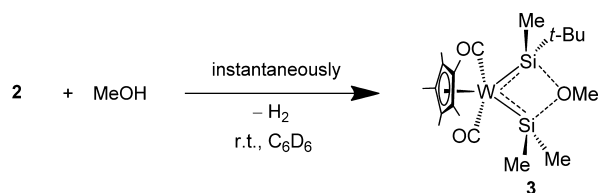


shifted $^1H$ NMR resonance for the bridging methoxy group (2.86 ppm).[9]

In summary, we have isolated hydrogen-bridged bis(silylene) complex **2**, as the first example of type **C** complex. This complex has a $WSi_2H$ four-membered-ring structure with a short diagonal Si−Si distance, which can be regarded as a snapshot of a transition state for 1,3-hydrogen migration on silyl(silylene) complexes. A novel multicenter bond consisting of a four-center interaction and a 3c-2e interaction at the $WSi_2H$ moiety of the complex was characterized by multiple NMR measurements, X-ray diffraction study, and DFT theoretical calculations. Further investigations on reactivity and dynamic behavior of **2** are in progress.

## ASSOCIATED CONTENT

**Ⓢ Supporting Information**

Experimental procedures, characterization data, X-ray crystallographic data, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

**Corresponding Authors**
hhashimoto@m.tohoku.ac.jp
tobita@m.tohoku.ac.jp

**Notes**
The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

## REFERENCES

(1) (a) Chauvin, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 3741−3747. (b) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748−3759. (c) Grubbs, R. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 3760−3765.

(2) (a) Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846−1855. (b) Thompson, M. E.; Baxer, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203−219.

(3) (a) Tobita, H.; Ueno, K.; Ogino, H. *Chem. Lett.* **1986**, 1777−1780. (b) Tobita, H.; Ueno, K.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2797−2804.

(4) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. P. *Organometallics* **1986**, *5*, 1056−1057.

(5) Silyl(silylene) complexes were first postulated as key intermediates in the reactions such as redistribution and oligomerization of hydrosilanes in 1970s. Ojima, I.; Inaba, S.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1973**, *55*, C7−C8.

(6) Tobita, H.; Matsuda, A.; Hashimoto, H.; Ueno, K.; Ogino, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 221−224.

(7) (a) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *110*, 4092−4093. (b) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415−3420.

(8) For reviews, see (a) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213−255. (b) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. (c) Ogino, H. *Chem. Rec.* **2002**, *2*, 291−306. (d) Okazaki, M.; Tobita, H.; Ogino, H. *Dalton Trans.* **2003**, 493−506.

(9) See Supporting Information for details.

(10) (a) Mork, B. V.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 9702−9703. (b) Ueno, K.; Asami, S.; Watanabe, N.; Ogino, H. *Organometallics* **2002**, *21*, 1326−1328. (c) Watanabe, T.; Hashimoto, H.; Tobita, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 218−221. (d) Takanashi, K.; Lee, V. Y.; Yokoyama, T.; Sekiguchi, A. *J. Am. Chem. Soc.* **2009**, *131*, 916−917.

(11) Ueno, K.; Masuko, A.; Ogino, H. *Organometallics* **1997**, *16*, 5023−5026.

(12) These values were well reproduced by theoretical calculations (see Table S4 in SI).

(13) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151−187.

(14) Kaftory, M.; Kapon, M.; Botashansky, M. *The Chemistry of Organic Silicon Compounds*, Vol. 2; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; part 1, Chapter 5.

(15) Ueno, K.; Tobita, H.; Ogino, H. *J. Organomet. Chem.* **1992**, *430*, 93−104.

(16) We observed a set of very broad satellite with $J$(Si−H) = 23 Hz for the ^{1}H NMR resonance of SiHSi at 2.92 ppm by the ^{1}H homodecoupling experiment, in spite of the existence of two inequivalent Si neclei in **2**. Judging from the intensity of the satellite signals, this is obviously caused by the overlap of two sets of them. We also tried to measure the $J$(Si−D) values of **2**-*d* because $J$(Si−H) values can be estimated from the corresponding $J$(Si−D) values by multiplying the ratio of the gyromagnetic ratios $\gamma H/\gamma D$ (= 6.51). The $J$(Si−H) for H···SiMe$_2$ was estimated to be 27.3 Hz from the $J$(Si−D) (4.2 Hz) observed for the resonance of SiMe$_2$ in **2**-*d* in the $^{29}$Si{$^1$H} NMR spectrum. The $J$(Si−H) value for H···SiMe(*t*-Bu) could not be determined because $J$(Si−D) was not clearly observed for the signal of SiMe(*t*-Bu) in **2**-*d*.

(17) Yokelson, H. B.; Millevolte, A. J.; Adams, B. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 4116−4118.

(18) Marsmann, H. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfield, R., Eds.; Springer-Verlag: Berlin and New York, 1981; Vol. *17*, p 128.

(19) For a related base-stabilized bis(silylene) iron complex, it was concluded that there is no direct Si−Si interaction based on the $J$(Si−Si) value and Extended Hückel MO calculations as reported in ref 15.

(20) (a) Sakaba, H.; Yoshida, M.; Kabuto, C.; Kabuto, K. *J. Am. Chem. Soc.* **2005**, *127*, 7276−7277. (b) Ray, M.; Nakao, Y.; Sato, H.; Sakaba, H.; Sakaki, S. *J. Am. Chem. Soc.* **2006**, *128*, 11927−11939.

(21) A similar four-membered-ring structure has been theoretically predicted to be stable in an iridium system, but detailed analysis including molecular orbital and NBO analysis for this system has not been reported. Besora, M.; Maseras, F.; Lledós, A.; Eisenstein, O. *Organometallics* **2006**, *25*, 4748−4755.