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Reactions of a hydrido(hydrosilylene)tungsten complex with oxiranes

Hisako Hashimoto *, Mitsuyoshi Ochiai, Hiromi Tobita

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

Abstract

Reactivity of a hydrido(hydrosilylene)tungsten complex, $Cp^*(CO)_2(H)W=Si(H)[C(SiMe_3)_3]$ (**1**), toward oxiranes was investigated. Treatment of **1** with racemic mono-substituted oxiranes with a substituent R (R = Ph, vinyl, ^tBu, or ^nBu) at room temperature produced dihydrido(vinyloxysilyl)tungsten complexes, (*E*)- and/or (*Z*)-$Cp^*(CO)_2(H)_2W\{Si(H)(OCH=CHR)[C(SiMe_3)_3]\}$ [(*E/Z*)-**2**: R = Ph, (*E*)-**3**: R = vinyl, (*E*)-**4**: R = ^tBu, (*E/Z*)-**5**: R = ^nBu] in high yields via regioselective ring-opening of oxiranes. When the substituent R on oxirane was relatively large, (*E*)-isomers (**2**, **3**, and **4**) were obtained predominantly (87–97%), while the substituent was a relatively small ^nBu group, an approximately 1:1 mixture of (*E*)- and (*Z*)-isomers [(*E/Z*)-**5**] was obtained. Reaction of **1** with 2,2-dimethyloxirane afforded the corresponding complex, $Cp^*(CO)_2(H)_2W\{Si(H)(OCH=CMe_2)[C(SiMe_3)_3]\}$ (**6**), quantitatively. A reaction mechanism is also discussed.
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1. Introduction

The chemistry of transition-metal silylene complexes has been extensively studied since they have been proposed to play important roles in various reactions of silicon compounds [1–8]. Although the well-defined reactions of isolated silylene complexes have been limited to the addition of nucleophiles such as water and alcohol to the highly polarized $M(\delta-)$–$Si(\delta+)$ double bonds [1c,1d], a number of recent efforts have started to open a new stage of reaction chemistry of silylene complexes [9–17]. Thus, it was found that silylene complexes having a M–H bond and/ or a Si–H bond showed high reactivities toward unsaturated organic compounds. For example, Tilley et al. reported that $[Cp^*(Me_3P)(H)Ir=SiPh_2][B(C_6F_5)_4]$ underwent catalytic hydrosilylation of ketone [11]. They also reported hydrosilylation of olefin catalyzed by $[Cp^*(^iPr_3-P)(H)_2Ru=Si(H)Ph][B(C_6F_5)_4]$ [12]. The mechanism of the former is not clear but a new mechanism consisting of direct addition of a Si–H bond to the double bond of olefin is suggested for the latter.

Our group recently succeeded in synthesizing $Cp^*(CO)_2(H)W=Si(H)[C(SiMe_3)_3]$ (**1**) and reported its stoichiometric hydrosilylation to acetone [15] and nitriles [17], which are usually resistant to hydrosilylation. We also suggested a mechanism for our system, in which the reactions are initiated by coordination of a heteroatom (O or N) of ketones and nitriles to the silicon center, followed by H-migration from W–H to the coordinated substrates, based on the structures of isolated intermediates [17]. These results prompted us to further investigate the reactivities of silylene complexes having M–H and Si–H bonds toward polar substrates having a lone pair. This time, we performed the reactions of **1** with oxiranes, which had not been used as reactants for silylene complexes before. We were interested in the similarities and differences of the behaviors between oxiranes and ketones in the reactions with **1**. Here, we report the reactions of **1** with various mono-substituted oxiranes and 2,2-dimethyloxirane. The reaction mechaism as well as regio- and stereoselectivity of the products are discussed.

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* Corresponding authors.
  E-mail address: hhashimoto@mail.tains.tohoku.ac.jp (H. Hashimoto).

2. Results and discussion

2.1. Reaction of $Cp^*(CO)_2(H)W=Si(H)[C(SiMe_3)_3]$ (1) with 2-phenyloxirane

Complex **1** reacted instantaneously with racemic 2-phenyloxirane at room temperature to afford a dihydrido(styryloxysilyl)tungsten complex, (E)-Cp*(CO)₂(H)₂W-{Si(H)(OCH=CHPh)[C(SiMe₃)₃]} [(E)-**2**], in 85% NMR yield and a minor product (Eq. (1)). Complex (E)-**2** was thermally unstable in solution but was isolated in 54% yield as yellow crystals by recrystallization at low temperature and fully characterized by spectroscopic data (as described below) and elemental analysis. The minor product was assigned to be a (Z)-isomer of **2** based on the ^{1}H NMR data, but it was not able to be fully characterized because of its low yield (<15%) and extreme thermal instability.

It is interesting that the ring of 2-phenyloxirane is opened regioselectively with forming a carbon–carbon double bond in this reaction. This kind of reaction by silylene complexes has never been reported. As a slightly related work, Weber et al. previously reported that $Co_2(CO)_8$ catalyzed a reaction of 2-phenyloxirane with trialkylsilane under CO to yield a mixture of (E/Z)-PhCH=CHOSiR₃ and PhCH₂CH₂O-SiR₃(SiR₃ = SiEt₃ or SiMe₂'Bu) [18]. In our system, we were not able to observe a similar compound (E/Z)-PhCH=CHOSiH₂[C(SiMe₃)₃], which might be reductively eliminated from (E/Z)-**2** in some specific conditions. Thermal decomposition of (E/Z)-**2** or use of excess 2-phenyloxirane and hydrosilane gave only a complex mixture.

(1)
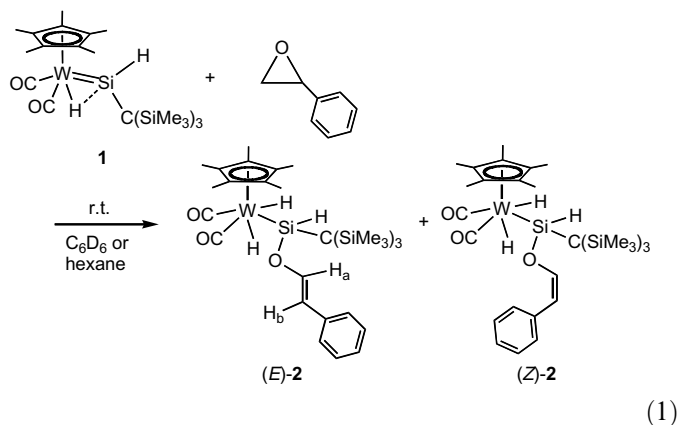
2.2. Characterization of product 2

In the ^{1}H NMR spectrum of (E)-**2**, signals for W–H and Si–H groups are observed at −6.68 and 7.23 ppm in the intensity ratio of 2:1 as doublet and triplet, respectively, coupled each other with $^3J_{HH} = 2.4$ Hz. A satellite coupling by the W atom ($^1J_{WH} = 47.8$ Hz) is observed for the former. Two W–H groups should be diastereotopic due to a chiral silicon atom attached to the W atom, but a single signal with 2H intensity is observed for them at room temperature. This would be attributed to a certain fluxional behavior involving the hydrido ligands because

this signal became broad at low temperature, although a detail is not clear at present. Both two vinyl proton signals appear as doublets at 6.25 and 7.37 ppm, respectively. The $^3J_{HH}$ coupling constant (12.5 Hz) of them indicates its E-geometry: this value is comparable with those of usual (E)-isomers of olefins [19] but is larger than those of the (Z)-isomers. It is also larger than that (7.0 Hz) of presumed (Z)-**2**. The ^{29}Si signals for SiH and SiMe₃ appear in a normal region for these groups in the ^{29}Si NMR spectrum. All ^{13}C NMR signals observed at −30 °C also agree with this structure. For example, two mutually diastereotopic CO ligands show signals inequivalently at 221.3 and 225.9 ppm. Two vinyl carbon signals appear at 109.8 and 143.7 ppm. The former is assigned to the carbon substituted by a Ph group and the latter to that substituted by a siloxy group. In addition, the IR spectrum of (Z)-**2** in CD₂Cl₂ reasonably show four strong peaks in 1898–1996 cm⁻¹ assigned to two v_{CO} and two v_{WH} as well as a weak peak for v_{SiH} at 2073 cm⁻¹, while the spectrum measured by KBr pellet show many peaks in 1830–1994 cm⁻¹ and two weak peaks in a region of v_{SiH}. This is probably caused by a packing effect in the solid state.

The structure of (E)-**2** was further supported by an X-ray crystal structure determination. In spite of a number of trials, we only obtained some needle crystals. Therefore, the quality of the crystals was not high enough for detailed discussions about the bond distances (as described in the experimental section), but we could figure out the overall structure. The ORTEP drawing of (E)-**2** is depicted in Fig. 1 with selected bond lengths and angles. The positions of hydrogen atoms were not determined but wide bond angles, Si1–W1–C20 [113.3(5)°] and Si1–W1–C19 [106.0(4)°], compared with the rest [C19–W1–C20: 84.4(7)°] suggest that there must be two hydrido ligands in these open sites. As a result, this complex adopts a rare five-legged piano-stool structure consisting of two CO, two H, and a silyl group. (E)-geometry of this complex is determined by the angles around the C–C double bond of the vinyl group. Thus, the bond angles of O1–C1–C2 and C1–C2–C3 are 123.7(13)° and 122.4(14)°, respectively. In addition, the atoms of O1, C1, C2, and C3 are almost within a plane.

2.3. Reactions of $Cp^*(CO)_2(H)W=Si(H)[C(SiMe_3)_3]$ (1) with other oxiranes and stereoselectivity of the products

When racemic 2-vinyloxirane or 2-t-butyloxirane was used as a reactant, only E-isomer, (E)-Cp*(CO)₂(H)₂W{Si-(H)(OCH=CHR)[C(SiMe₃)₃]} [(E)-**3**: R = vinyl (97%), (E)-**4**: R = 'Bu (89%); yields determined by NMR], was produced and its (Z)-isomer was not clearly detected by ^{1}H NMR spectroscopy (Eqs. (2) and (3)). Complex (E)-**3** was relatively stable and isolated in 79% yield, while (E)-**4** was fairly unstable and isolated in 31% yield. Even during recrystallization at low temperature, (E)-**4** slowly decomposed to give a complex mixture, which could not be identified. In the case of racemic 2-n-butyloxirane, a similar reaction afforded an approximately 1:1 mixture of (E/Z)-

isomers, (E/Z)-Cp*(CO)$_2$(H)$_2$W{Si(H)(OCH=CH^{n}Bu)[C-(SiMe$_3$)$_3$]} [(E/Z)-**5**] (Eq. (4)). (E)-isomers of **3**–**5** and (Z)-**5** were fully characterized based on the similarity of their spectroscopic data to those of (E)-**2** except the $^3J_{HH}$ coupling constant between two vinyl protons of (Z)-**5**. The $^3J_{HH}$ (6.2 Hz) of (Z)-**5** is significantly smaller than those of (E)-isomers ($\sim$12 Hz) and close to that of (Z)-**2** (7.0 Hz). The X-ray crystal structure of (Z)-**5** shown in Fig. 2 also supports its (Z)-geometry, though the quality of data is not very high [for detail, see Section 4].

Finally, we performed the reaction of **1** with 2,2-dimethyloxirane to produce Cp*(CO)$_2$(H)$_2$W{Si(H)(OCH=CMe$_2$)-C(SiMe$_3$)$_3$]} (**6**) as a sole product, quantitatively (Eq. (5)).

(2)

(3)

(4)

(5)
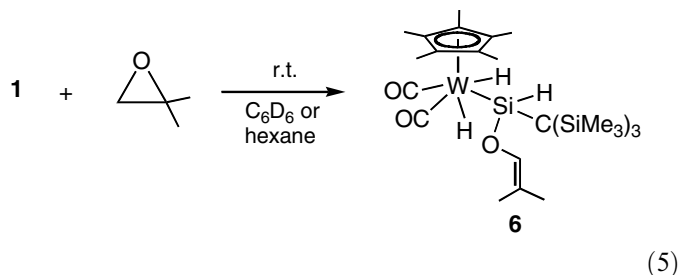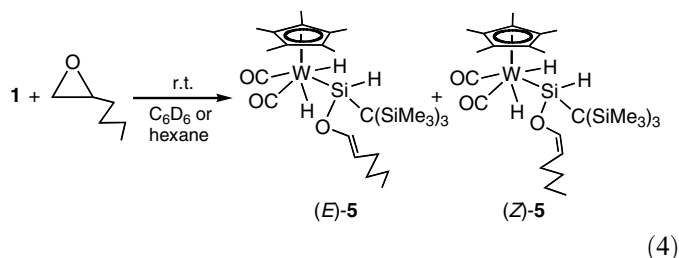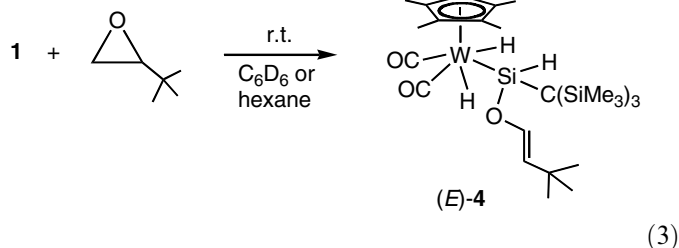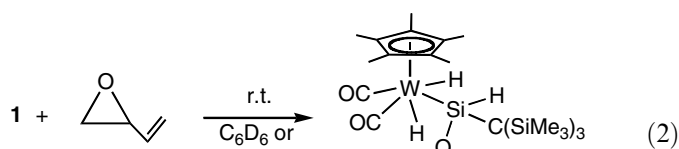
All results of the reactions are summarized in Table 1. From this table, the following points are obvious. Firstly, the C–C bond cleavage of oxiranes occurs regioselectively so that the substituents are positioned at the β-carbon of the resulting vinyl groups of the products. Secondly, in the case of oxiranes having relatively large substituents, (E)-isomers (**2**, **3**, and **4**) predominantly formed.
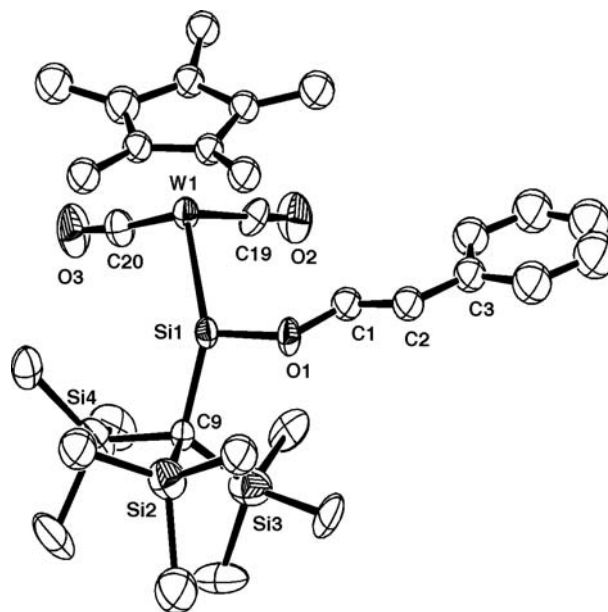

Fig. 1. ORTEP drawing of (E)-Cp*(CO)$_2$(H)$_2$W{Si(H)(OCH=CHPh)-[C-(SiMe$_3$)$_3$]} [(E)-**2**] Thermal ellipsoids are drawn at the 30% probability. Selected bond lengths (Å) and angles (°): W1–Si1 = 2.567(3), Si1–O1 = 1.676(9); and Si1–W1–C19 = 106.0(4), Si1–W1–C20 = 113.3(5), C19–W1–C20 = 84.4(7), O1–C1–C2 = 123.7(13), C1–C2–C3 = 122.4(14).
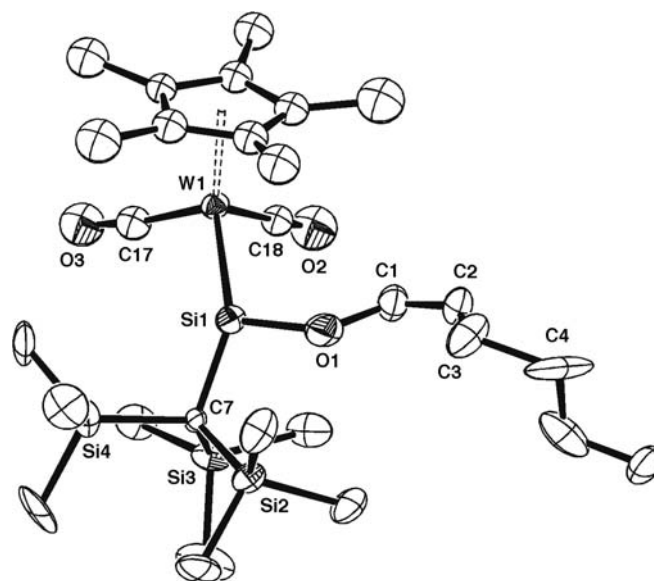

Fig. 2. ORTEP drawing of (Z)-Cp*(CO)$_2$(H)$_2$W{Si(H)(OCH=CHCH$_2$-CH$_2$CH$_2$CH$_3$)C(SiMe$_3$)$_3$]} [(Z)-**5**]. Thermal ellipsoids are drawn at the 50% probability. Selected bond lengths (Å) and angles (°): W1–Si1 = 2.576(4), Si1–O1 = 1.702(13); and Si1–W1–C17 = 110.6(6), Si1–W1–C18 = 109.8(5), O1–C1–C2 = 121(2), C1–C2–C3 = 128(2).

2.4. Possible reaction mechanisms

Possible reaction mechanisms for the reactions of **1** with racemic oxiranes are illustrated in Scheme 1. First of all, complex **1** has optical isomers of clockwise (*C*-isomer) and anticlockwise (*A*-isomer) [20] as described in Chart 1. In addition, the hydrido group bridges over the W=Si bond. As the reaction with *A*-isomer of **1** (*A*-**1**) is thought

Table 1
Summary of the reactions of **1** with oxiranes

Entry	Oxirane	Time[a]	Product NMR yield (isolated yield) (%)	
			E	Z
1		Instantaneous	87 (54)	<15
			(E)-**2**	(Z)-**2**
2		Instantaneous	97 (79)	
			(E)-**3**	
3		1 h[b]	87[c] (31)	
			(E)-**4**	
4		3 h	27[d]	34[d] (27)
			(E)-**5**	(Z)-**5**
5		Instantaneous	100 (29)	
			6	

[a] In hexane.
[b] In toluene.
[c] Yield based on consumed **1** (conversion 66%).
[d] Yield based on consumed **1** (conversion 70%).

to proceed in a mirror image to the reaction with *C*-isomer
(*C*-**1**), mechanisms for *C*-**1** are discussed in detail here. The
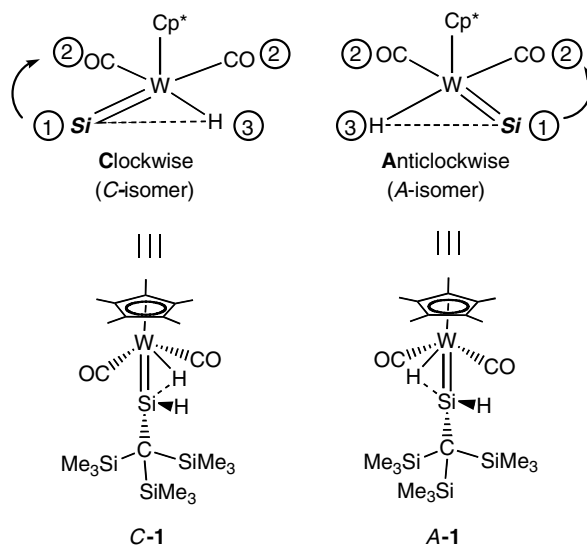initial step must be coordination of a lone pair of oxirane

Chart 1.

to the silylene silicon atom as we have previously suggested
for the reactions of **1** with ketones and nitriles [15,17]. In
this step, it is reasonably postulated that oxiranes can
approach to the silylene ligand only from the side where
the hydrido ligand doesn't bridge over the W≡Si bond
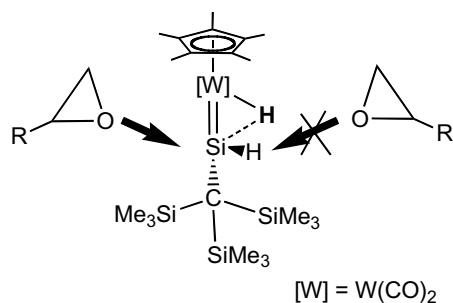(Chart 2). As we used an *R/S*-mixture of mono-substituted
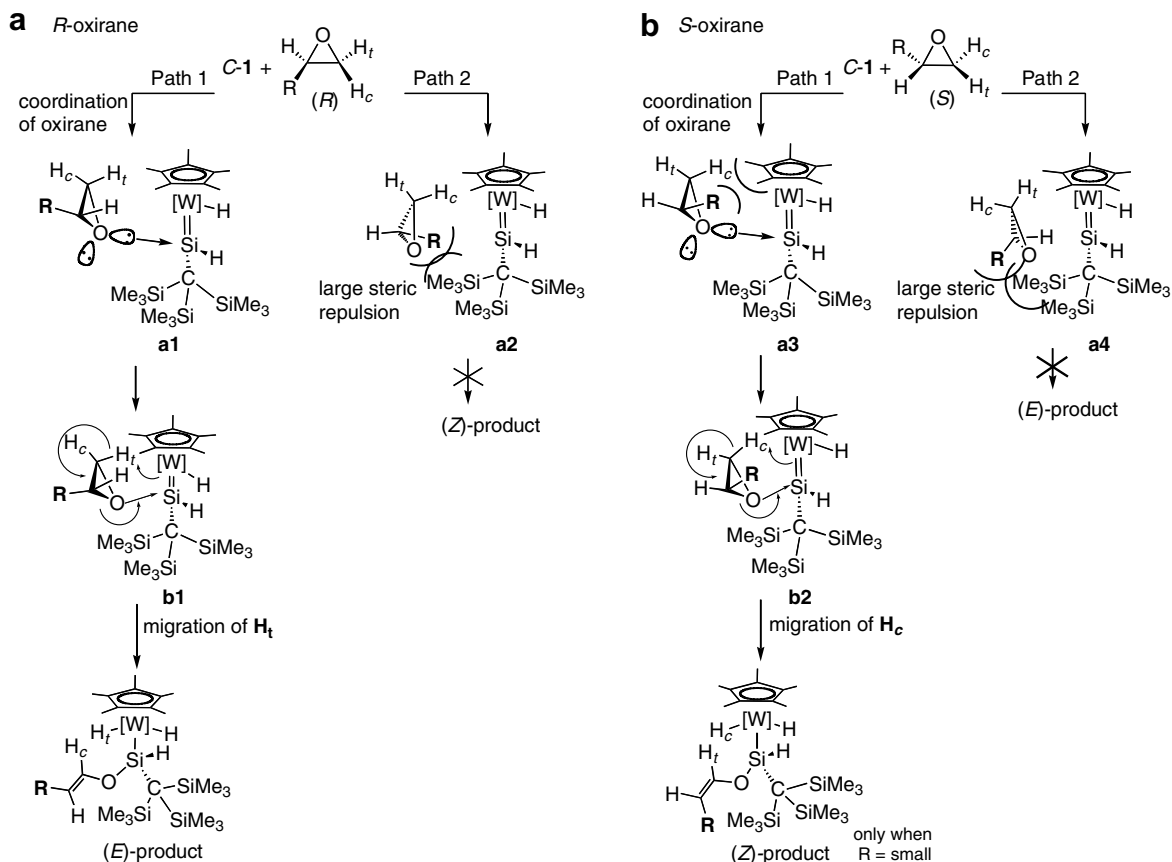
Scheme 1.

Chart 2.

oxiranes, we need to consider the reactions with both *R*- and *S*-oxirane [(a) and (b) in Scheme 1]. Furthermore, there are two possible orientations for coordination of oxiranes. Path 1 shows a case where the oxygen atom of oxirane takes the position below its C–C bond when the C–C bond is positioned parallel to the W=Si bond. Path 2 shows a case where the oxygen atom takes the position above its C–C bond. Therefore, when *R*-oxirane approaches to *C*-**1** through Path 1, a lone pair of O atom can be coordinated to the silylene silicon atom like **a1**. It is likely here that the hydrido ligand bridging over the W=Si bond moves to a terminal position. By coordination of the oxirane, the H_t atom positioned *trans* to the substituent R on oxirane is forced to be close to the W center (**b1**). Then, the H_t atom migrates to the W atom and subsequent C–O bond cleavage (near R) and a C–C double bond formation occur to produce (*E*)-product. If the reaction could proceed through Path 2 in a similar way, the H_c atom positioned *cis* to R would migrate to the W atom to produce (*Z*)-product. However, because of large steric repulsion between R and the C(SiMe₃)₃ group, this Path 2 is not likely to be selected. When *S*-oxirane approaches to *C*-**1** through Path 1, (*Z*)-product could be produced via intermediates **a3** and **b2** in a similar way. However, in this case, when R is large, steric repulsion between the R and the C(SiMe₃)₃ group becomes large in **a3** and **b2**. Therefore, when R is small like a *n*-butyl group, the reaction can proceed through this path to give (*Z*)-product. It is also not likely that the reaction of *C*-**1** and *S*-oxirane proceeds through Path 2 to generate (*E*)-isomer because of large steric repulsion between the R and the C(SiMe₃)₃ group in **a4**. As a result, when R on oxirane is large, (*E*)-isomer is selectively generated through Path 1 by the reaction of *C*-**1** and *R*-oxirane. In a mirror image, the reaction of *A*-**1** with *S*-oxirane can also produce (*E*)-isomer selectively through Path 1 when R is large. When R is small, (*Z*)-isomer is additionally generated by the combinations of *C*-**1** and *S*-oxirane or *A*-**1** and *R*-oxirane through Path 1.

3. Conclusion

It was found that a hydrido(hydrosilylene) tungsten complex, Cp*(CO)₂(H)W=Si(H)[C(SiMe₃)₃] (**1**), smoothly

reacted with racemic oxiranes with a substituent R (R = Ph, vinyl, *t*Bu, or *n*Bu) and also 2,2-dimethyloxirane to produce Cp*(CO)₂(H)₂W[Si(H)(OCH=CHR){C-(SiMe₃)₃}] [(*E/Z*)-**2**: R = Ph, (*E*)-**3**: R = vinyl, (*E*)-**4**: R = *t*Bu, (*E/Z*)-**5**: R = *n*Bu] and Cp*(CO)₂(H)₂W{Si-(H)(OCH=CMe₂)[C(SiMe₃)₃]} (**6**), regioselectively in high yields. Possible reaction mechanisms are suggested to involve: (1) coordination of a lone pair of oxiranes to the silylene silicon atom, (2) H-migration from the coordinated oxirane to the ruthenium atom, (3) regioselective ring-opening of the oxirane, and (4) formation of a vinyl group. (*E*)- or (*Z*)-selectivity of the product is mainly controlled by the bulkiness of the substituent R on mono-substituted oxiranes. When R is large, (*E*)-isomer is predominantly produced through the combinations of *C*-**1** (clockwise isomer of **1**) and *R*-oxirane or *A*-**1** (anticlockwise isomer of **1**) and *S*-oxirane. Further reactivity studies of **1** are under way.

4. Experimental

4.1. General procedure

4.2. Reactions of Cp*(CO)₂(H)W=Si(H)[C(SiMe₃)₃] (**1**) with 2-phenyloxirane

4.2.1. NMR experiment

In an NMR tube having a screw cap and rubber septum on the top, a benzene-d_6 solution of Cp*(CO)₂(H)W=Si(H)[C(SiMe₃)₃] (**1**) (10 mg, 0.016 mmol) containing hexamethylbenzene (~2 mg) as an internal standard was prepared. After the ¹H NMR spectrum of the solution was

measured, 2-phenyloxirane (1.4 µl, 0.018 mmol) was added to it by a microsyringe at room temperature. The ^{1}H NMR spectrum of the solution measured again showed the signals for (E)-Cp*(CO)$_2$(H)$_2$W{Si(H)(OCH=CHPh)[C(SiMe$_3$)$_3$] [(E)-**2**] in 85% yield and a minor product. The minor product is suggested to be (Z)-Cp*(CO)$_2$(H)$_2$W{Si(H)(OCH=CHPh)[C(SiMe$_3$)$_3$] [(Z)-**2**] (<15%) based on the ^{1}H NMR data.

4.2.2. Isolation of (E)-2

In a Pyrex glass tube ($\phi = 2$ cm, 17 cm) equipped with a Teflon needle valve on the top, hexane was added to **1** (50 mg, 0.079 mmol) by trap-to-trap transfer method. To the solution was added 2-phenyloxirane (6.9 µl, 0.086 mmol) at room temperature and the mixture was stirred for 5 min. After filtration, volatiles were removed under vacuum. The resulting residues were recrystallized from pentane at −30 °C to afford (E)-**2** as yellow crystals in 54% yield (32 mg, 0.042 mmol). A minor product, (Z)-**2**, could not be isolated because it was very unstable in solution and repeated recrystallization caused decomposition.

(E)-**2**: ^{1}H NMR (300 MHz, C$_6$D$_6$, δ) −6.68 (d, $^3J_{HH}$ = 2.4 Hz, $^2J_{WH}$ = 47.8 Hz, 2H, WH), 0.51 (s, 27H, SiMe), 1.70 (s, 15H, C$_5$Me$_5$), 6.25 (d, $^3J_{HH}$ = 12.5 Hz, 1H, C*H*Ph), 6.96 (tt, $^3J_{HH}$ = 7.27 Hz, $^4J_{HH}$ = 1.21 Hz, 1H, *p*-H of Ph), 7.10 (virtual t, 2H, *m*-H of Ph), 7.23 (t, 1H, SiH, $^3J_{HH}$ = 2.4 Hz), 7.33 (virtual d, 2H, *o*-H of Ph), 7.37 (d, $^3J_{HH}$ = 12.5 Hz, 1H, SiOC*H*). ^{13}C{^{1}H} NMR (75.5 MHz, CD$_2$Cl$_2$, −30 °C δ) 4.2 (Si*Me*), 6.8 (*C*(SiMe$_3$)$_3$), 10.8 (C$_5$*Me*$_5$), 101.3 (*C*$_5$Me$_5$), 109.8 (*C*HPh), 124.2, 124.9, 128.4, 137.0 (Ph), 143.7 (SiO*C*), 221.3 (*C*O), 225.9 (*C*O). ^{29}Si{^{1}H} NMR (59.6 MHz, C$_6$D$_6$ δ) −0.5 (Si*Me*), 14.2 (Si*H*). IR (CD$_2$Cl$_2$, cm^{-1}): 2073 (w, SiH), 1996 (vs), 1967 (vs), 1919 (vs), 1898 (vs) (CO, WH). IR (KBr pellet, cm^{-1}): 2115 (m), 2073 (sh) (SiH), 1994 (s), 1963 (vs), 1917 (sh), 1901 (vs), 1874 (sh), 1830 (sh) (CO, WH). Exact Mass (ESI, negative): Calc. for [C$_{30}$H$_{52}$O$_3$Si$_4$W–H]$^-$: 755.2431. Found: 755.2433.

Anal. Calc. for C$_{30}$H$_{52}$O$_3$Si$_4$W: C, 47.60; H, 6.92. Found: C, 47.79; H, 7.01%.

(Z)-**2**: ^{1}H NMR (300 MHz, C$_6$D$_6$, δ): −7.03 (d, $^3J_{HH}$ = 1.5 Hz, $^2J_{WH}$ = 45.7 Hz, 2H, WH), 0.46 (s, 27H, SiMe$_3$), 1.71 (s, 15H, Cp*), 5.35 (d, $^3J_{HH}$ = 7.0 Hz, 1H, C*H*Ph), 6.70 (d, $^3J_{HH}$ = 7.0 Hz, 1H, OC*H*). The SiH and Ph signals could not be assigned because they are overlapped with the signals of (E)-**2**.

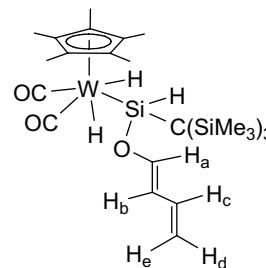### 4.3. Reactions of Cp*(CO)$_2$(H)W=Si(H)[C(SiMe$_3$)$_3$] (1) with 2-vinyloxirane

4.3.1. NMR experiment

In a procedure similar to that described in Section 4.2.1, **1** (8 mg, 0.01 mmol) and 2-vinyloxirane (1.2 µl, 0.015 mmol) was mixed in benzene-d_6 at room temperature. The ^{1}H NMR spectrum showed the immediate formation of (E)-Cp*(CO)$_2$(H)$_2$W{Si(H)(OCH=CHCH=CH$_2$)[C(SiMe$_3$)$_3$]} [(E)-**3**] in 97% yield.

4.3.2. Isolation of (E)-3

In a procedure similar to that described in Section 4.2.2, from **1** (73 mg, 0.12 mmol) and 2-vinyloxirane (11 µl, 0.14 mmol), E-**3** was isolated in 79% yield (64 mg, 0.091 mmol).

(E)-**3**: ^{1}H NMR (300 MHz, C$_6$D$_6$, δ) −6.76 (d, $^3J_{HH}$ = 2.6 Hz, $^2J_{WH}$ = 47.7 Hz, 2H, WH), 0.47 (s, 27H, SiMe), 1.70 (s, 15H, C$_5$Me$_5$), 4.84 (dd, $^2J_{HH}$ = 1.8 Hz, $^3J_{HH}$ = 9.9 Hz, 1H, CH$_d$), 5.04 (dd, $^2J_{HH}$ = 1.83 Hz, $^3J_{HH}$ = 16.8 Hz, 1H, CH$_e$), 5.99 (t, $^3J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 12.1 Hz, 1H, CH$_b$), 6.26 (m, 1H, CH$_c$), 6.79 (d, $^3J_{HH}$ = 12.1 Hz, 1H, CH$_a$), 7.13 (t, 1H, SiH, $^3J_{HH}$ = 2.6 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, toluene-d_8, −30 °C δ) 4.9 (Si*Me*), 7.2 (*C*(SiMe$_3$)$_3$), 10.4 (C$_5$*Me$_5$), 101.4 (*C*$_5$Me$_5$), 111.2, 113.3, 134.2 (*C*HCHCH$_2$), 146.8 (SiO*C*), 221.1 (*C*O), 225.7 (*C*O). ^{29}Si{^{1}H} NMR (59.6 MHz, C$_6$D$_6$, δ) −0.6 (Si*Me*), 13.8 (Si*H*). IR (toluene-d_8, cm^{-1}): 2073 (w, SiH), 1998 (vs), 1969 (vs), 1923 (vs), 1900 (vs) (CO, WH). IR (KBr pellet, cm^{-1}): 2102 (m), 2085 (m) (SiH), 1994 (vs), 1961 (vs), 1928 (vs), 1898 (vs) (CO, WH). Exact Mass (ESI, negative): Calc. for [C$_{26}$H$_{50}$O$_3$Si$_4$W–H]$^-$: 705.2274. Found: 705.2277. Anal. Calc. for C$_{26}$H$_{50}$O$_3$Si$_4$W: C, 44.18; H, 7.13. Found: C, 43.78; H, 7.21%.

4.4. Reactions of Cp*(CO)$_2$(H)W=Si(H)[C(SiMe$_3$)$_3$] (1) with 2-t-butyloxirane

4.4.1. NMR experiment

In a procedure similar to that described in Section 4.2.1, the reaction of **1** (10 mg, 0.016 mmol) and 2-*t*-butyloxirane (2.5 µl, 0.021 mmol) was monitored by ^{1}H NMR spectroscopy. The reaction was slow and before **1** was consumed completely, a product, (E)-Cp*(CO)$_2$(H)$_2$W{Si(H)(OCH=CH^{t}Bu)[C(SiMe$_3$)$_3$]} [(E)-**4**], started to decompose. The maximum conversion yield of (E)-**4** was 87% after 66% conversion in 5 h.

4.4.2. Isolation of (E)-4

In a procedure similar to that described in Section 4.2.2, a toluene solution of **1** (100 mg, 0.160 mmol) and 2-*t*-butyloxirane (146 µl, 1.19 mmol) was stirred for 1 h at room temperature. (E)-**4** was isolated in 31% yield (36 mg, 0.049 mmol) by recrystallization at −30 °C.

(E)-**4**: ^{1}H NMR (300 MHz, cyclohexane-d_{12}, δ) −6.99 (d, $^3J_{HH}$ = 2.6 Hz, $^2J_{WH}$ = 47.9 Hz, 2H, WH), 0.27 (s, 27H, SiMe), 1.17 (s, 8H, ^{t}Bu), 2.08 (s, 15H, C$_5$Me$_5$), 4.92 (d,

$^3J_{HH} = 12.1$ Hz, 1H, OCHCH), 6.18 (d, $^3J_{HH} = 12.1$ Hz, 1H, OCHCH), 6.86 (t, $^3J_{HH} = 2.6$ Hz, $^1J_{SiH} = 225.4$ Hz, 1H, SiH). ^{13}C{^{1}H} NMR (75.5 MHz, toluene-d_8, −30 °C, δ) 4.9 (SiMe), 7.4 (C(SiMe$_3$)$_3$), 10.4 (C_5Me_5), 30.6, 31.3 (^tBu), 101.5 (C_5Me_5), 121.0 (CH^tBu), 138.8 (SiOC), 222.0 (CO), 226.6 (CO). ^{29}Si{^{1}H} NMR (59.6 MHz, cyclohexane-d_{12}, δ) −5.0 (SiMe), 14.7 (SiH). IR (toluene-d_8, cm^{-1}): 1996 (vs), 1965 (vs), 1921 (vs), 1898 (vs) (CO, WH). IR (KBr pellet, cm^{-1}): 2112 (w, SiH), 1992 (m), 1965 (vs), 1927 (m), 1897 (vs), 1876 (sh), 1857 (m) (CO, WH). Exact Mass (ESI, negative): Calc. for [C$_{28}$H$_{56}$O$_3$Si$_4$W–H]$^-$: 735.2744. Found: 735.2739. Anal. Calc. for C$_{28}$H$_{56}$O$_3$Si$_4$W: C, 45.64; H, 7.66%. Found: C, 45.69; H, 7.36%.

4.5. Reactions of $Cp^*(CO)_2(H)W=Si(H)[C(SiMe_3)_3]$ (1) with 2-n-butyloxirane
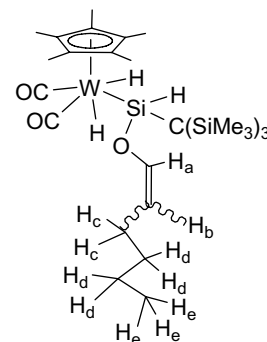
4.5.1. NMR experiment

In a procedure similar to that described in Section 4.2.1, the reaction of **1** (10 mg, 0.016 mmol) and 2-n-butyloxirane (2.3 µl, 0.019 mmol) in benzene-d_6 was monitored by ^{1}H NMR spectroscopy. (*E*)- and (*Z*)- isomers of Cp*(CO)$_2$-(H)$_2$W{Si(H)(OCH=CHCH$_2$CH$_2$CH$_2$CH$_3$)[C(SiMe$_3$)$_3$]} [(*E/Z*)-**5**] were observed in 27% and 34% conversion yields, respectively, after 70% conversion in 2 h at room temperature.

4.5.2. Isolation of (Z)-5

In a procedure similar to that described in Section 4.2.2, (*Z*)-**5** was isolated in 27% yield (19 mg, 0.026 mmol) by the reaction of **1** (60 mg, 0.094 mmol) and 2-n-butyloxirane (34 µl, 0.28 mmol) for 3 h, and recrystallization using hexamethyldisiloxane at −30 °C.

(*Z*)-**5**: ^{1}H NMR (300 MHz, C$_6$D$_6$, δ) −7.00 (d, $^3J_{HH} = 2.6$ Hz, $^2J_{WH} = 47.6$ Hz, 2H, WH), 0.49 (s, 27H, SiMe), 0.92–0.99 (m, 4H, H$_e$), 1.40–1.48 (m, 2H, H$_d$), 1.75 (s, 15H, Cp*), 2.28–2.40 (m, 2H, H$_c$), 4.52 (q, $^3J_{HH} = 6.2$ Hz, $^3J_{HH} = 7.0$ Hz, 1H, H$_b$), 6.45 (dt, $^3J_{HH} = 6.2$ Hz, $^4J_{HH} = 1.5$ Hz, 1H, H$_a$), 7.06 (t, $^3J_{HH} = 2.2$ Hz, $^1J_{SiH} = 226.9$ Hz, 1H, SiH). ^{13}C{^{1}H} NMR (75.5 MHz, toluene-d_8, −30 °C, δ) 4.8 (SiMe), 7.3 (C(SiMe$_3$)$_3$), 10.3 (C_5Me_5), 14.5, 23.3, 25.2, 32.5 (^nBu), 102.0 (C_5Me_5), 108.7 (CH^nBu), 139.8 (SiOC), 222.2 (CO), 226.6 (CO). ^{29}Si{^{1}H} NMR (59.6 MHz, toluene-d_8, −30 °C, δ) 8.0 (SiMe), 13.8 (SiH). IR (toluene-d_8, cm^{-1}) 2081 (w, SiH), 1996 (s), 1965 (vs), 1921 (s), 1898 (vs) (CO, WH). IR (KBr pellet, cm^{-1}): 2104 (w, SiH), 1996 (w), 1961 (vs), 1923 (m), 1900 (s), 1890 (vs) (CO, WH). Exact Mass (ESI, negative): Calc. for [C$_{28}$H$_{56}$O$_3$Si$_4$W–H]$^-$: 735.2744. Found: 735.2740.

(*E*)-**5**: ^{1}H NMR (300 MHz, C$_6$D$_6$, δ) −6.71 (d, $^3J_{HH} = 2.9$ Hz, $^2J_{WH} = 48.7$ Hz, 2H, WH), 0.50 (s, 27H, SiMe), 0.84–0.91 (m, 4H, H$_e$), 1.32–1.38 (m, 2H, H$_d$), 1.76 (s, 15H, Cp*), 5.14 (m, 1H, H$_b$), 6.46 (dt, $^3J_{HH} = 12.1$ Hz, $^4J_{HH} = 1.1$ Hz, 1H, H$_a$), 7.17 (t, $^3J_{HH} = 2.9$ Hz, 1H, SiH). The H$_c$ signal could not be assigned because they are overlapped with the signals of (*Z*)-**5**.

4.6. Reactions of $Cp^*(CO)_2(H)W=Si(H)[C(SiMe_3)_3]$ (1) with 2,2-dimethyloxirane

4.6.1. NMR experiment

In a procedure similar to that described in Section 4.2.1, the reaction of **1** (10 mg, 0.016 mmol) and 2,2-dimethyloxirane (2.1 µl, 0.023 mmol) was monitored by ^{1}H NMR spectroscopy. Instant and quantitative (∼100%) formation of Cp*(CO)$_2$(H)$_2$W{Si(H)(OCH=(CH$_3$)$_2$)[C(SiMe$_3$)$_3$]} (6) was observed.

4.6.2. Isolation of 6

In a procedure similar to that described in Section 4.2.2, **6** was isolated in 29% yield (28 mg, 0.039 mmol) by the reaction of **1** (87 mg, 0.13 mmol) and 2,2-dimethyloxirane (15.7 µl, 0.18 mmol) for 5 min, and recrystallization using hexamethyldisiloxane at −30 °C. The low isolation yield is due to the high thermal instability of **6** in solution.

6: ^{1}H NMR (300 MHz, C$_6$D$_6$, δ) −6.93 (d, $^3J_{HH} = 2.9$ Hz, $^2J_{WH} = 47.6$ Hz, 2H, WH), 0.49 (s, 27H, SiMe), 1.60 (d, $^4J_{HH} = 1.1$ Hz, 3H, Me), 1.73 (s, 15H, C$_5Me_5$), 1.80 (d, $^4J_{HH} = 1.1$ Hz, 3H, Me), 6.33 (m, 1H, OCH), 7.08 (t, $^3J_{HH} = 2.9$ Hz, $^1J_{SiH} = 225.8$ Hz, 1H, SiH). ^{13}C{^{1}H} NMR (75.5 MHz, CD$_2$Cl$_2$, −30 °C, δ) 4.1 (SiMe), 6.8 (C(SiMe$_3$)$_3$), 10.4 (C_5Me_5), 15.5, 19.5 (CMe$_2$), 102.5 (C_5Me_5), 109.7 (CMe$_2$), 134.8 (SiOC), 222.9 (CO), 227.1 (CO). ^{29}Si{^{1}H} NMR (59.6 MHz, C$_6$D$_6$, δ) −0.73 (SiMe), 11.1 (SiH). IR (CD$_2$Cl$_2$, cm^{-1}): 1994 (s), 1963 (vs), 1917 (s), 1892 (vs) (CO, WH). IR (KBr pellet, cm^{-1}): 2077 (m, SiH), 1986 (vs), 1967 (s), 1916 (vs), 1900 (s) (CO, WH). Exact Mass (ESI, negative): Calc. for [C$_{26}$H$_{52}$O$_3$Si$_4$W–H]$^-$: 707.2431. Found: 707.2434. Anal. Calc. for C$_{26}$H$_{50}$O$_3$Si$_4$W: C, 44.05; H, 7.39%. Found: C, 43.87; H, 7.23%.

4.7. X-ray crystal structure determinations of (E)-2 and (Z)-5

Diffraction measurements were made on a RIGAKU RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation. Single crystals of (*E*)-**2** and (*Z*)-**5** were coated with liquid paraffin and were mounted on a glass fiber. The structures were solved by Patterson and Fourier transform methods using SHELXS-97

[21] and refined by full matrix least-squares techniques on all F^2 data. A total of 44 images, corresponding to 220.0° oscillation angles, were collected with two different goniometer settings. Exposure time was 1.33 min per degree for (E)-**2** and 2.0 min per degree for (Z)-**5**. Readout was performed in the 0.100 mm pixel mode. Numerical absorption collections were made using the program NUMABS. In both cases of (E)-**2** and (Z)-**5**, some carbon atoms on the pentamethylcyclopentadienyl group and the tris(trimethyl)silyl group were refined with isotropic thermal parameters because attempts to refine them with anisotropic thermal ellipsoids led to non-positive definite ellipsoids. The other heavier atoms were refined with individual anisotropic thermal parameters. The positions of the hydrogen atoms of the W–H and the Si–H groups were not found from the Fourier-difference electron-density map. All other hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. For (E)-**2**, the final residue R_1 and the weighted wR_2 were $R_1 = 0.0674$ and $wR_2 = 0.1810$ for 6026 reflections with $I > 2\sigma(I)$. For (Z)-**5**, the final residue R_1 and the weighted wR_2 were $R_1 = 0.0742$ and $wR_2 = 0.1858$ for 6816 reflections with $I > 2\sigma(I)$. Crystallographic data of (E)-**2** and (Z)-**5** are shown in Tables S1-1 and S2-1, respectively, in the supporting information.

Acknowledgement

Appendix A. Supplementary material

Crystallographic Information has been deposited with the Cambridge Crystallographic Data Centre CCDC Nos. 299659 [(E)-**2**], 299660 [(Z)-**5**]. The data can be obtained free of charge via www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.071.

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