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Synthesis, structure, and reactivity of a pyridine-stabilized silanonetungsten complex†

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A pyridine-stabilized silanonetungsten complex $Cp^*(OC)_2W\{O{=}SiMes_2(py)\}(SiMe_3)$ (**1b**, $Cp^* = \eta^5\text{-}C_5Me_5$, Mes = 2,4,6-$Me_3C_6H_2$, py = C_5H_5N) was obtained by the reaction of a silyl(silylene) complex $Cp^*(OC)_2W({=}SiMes_2)(SiMe_3)$ (**3**) with pyridine-*N*-oxide in pyridine. X-ray crystal structure determination revealed that complex **1b** shows a similar geometry to that observed for a previously synthesized DMAP-stabilized analogue, $Cp^*(OC)_2W\{O{=}SiMes_2(DMAP)\}(SiMe_3)$ (**1a**, DMAP = 4-$NMe_2C_6H_4N$). The Si=O and W–O bond distances in **1b** are comparable to those observed in **1a**, but the nitrogen to silicon coordination bond of **1b** is slightly longer (*ca.* 0.05 Å) than that of **1a**, indicating the weaker coordination of pyridine than that of DMAP. The reaction of **1b** with excess PMe_3 in C_6D_6 at r. t. proceeded *via* elimination of pyridine to afford a five-membered metallacyclic carbene complex, $Cp^*(OC)W({=}C(SiMe_3)OSiMes_2O)(PMe_3)$ (**5**), but that of **1a** with PMe_3 did not proceed at all. Complex **5** was further transformed in C_7D_8 at 100 °C for 4 h to give a four-membered W–O–Si–O metallacyclic complex with carbyne and PMe_3 ligands, $Cp^*W(OSiMes_2O)({\equiv}CSiMe_3)(PMe_3)$ (**7**). The structural features of complexes **1b**, **5**, and **7** are comparable to those suggested theoretically as intermediates in the reaction of **3** with a sulfuration reagent to afford a six-membered metallacyclic carbene complex, $Cp^*W(S)\{{=}C(SiMe_3)C({=}O)OSiMes_2S\}$ (**6**), indicating that complex **1b** and the theoretically proposed silanethione complex are transformed *via* a similar reaction pathway.

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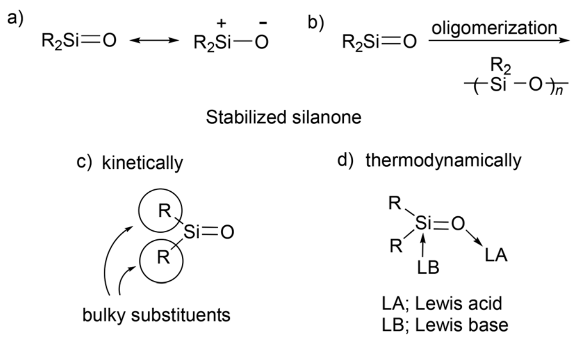
Introduction

The synthesis, structures and reactivity of silanones ($R_2Si{=}O$), a heavier congener of ketones ($R_2C{=}O$), have been studied intensively. Silanones have been known as highly reactive species due to the presence of a highly polarized Si=O bond as $Si^{\delta+}\text{–}O^{\delta-}$ (Pauling electronegativity; silicon 1.7 and oxygen 3.5) and an intrinsically weak π-bond (Scheme 1a) which cause spontaneous conversion to form a stable polysiloxane $(R_2SiO)_n$ (Scheme 1b).[1] Silanones have been investigated mainly by spectroscopic methods in inert matrices at low temperature,[2] however, a few examples have recently been isolated utilizing kinetic stabilization by bulky substituents on Si (Scheme 1c) and thermodynamic stabilization by Lewis base and/or Lewis acid coordination (Scheme 1d).[3–6]

The coordination of silanones to transition metal fragments to form silanone complexes is a reliable method for the stabilization of silanones (Scheme 2a). The chemistry of silanone complexes has recently attracted considerable attention from the viewpoint of not only bonding, structures and reactivity, but also the possibility of them being used as a reliable substrate and catalyst for the synthesis of organosiloxanes. Since the first isolation of a silanonezinc complex reported by Driess *et al.* in 2009,[7] five silanone complexes[7–9] have been reported to date, including three complexes **1a**, **2a**, and **2b**[8a,b] reported by our group (Scheme 2b).

The synthesis and structures of silanone complexes have been studied extensively, however, their reactivity has remained unexplored except for several reactions being reported by us.[8] Investigation on the reactivity of silanone



Scheme 1 (a) Silanone and its zwitterionic form, (b) formation of polysiloxane *via* oligomerization of silanone, (c) kinetically stabilized silanone by bulky substituents, and (d) thermodynamically stabilized silanone by Lewis acid and base.

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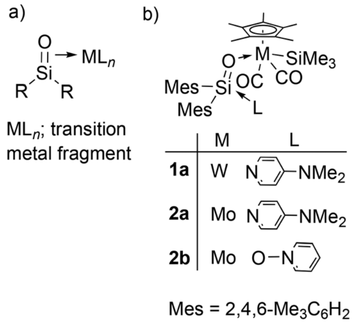


Scheme 2 (a) Schematic representation of the $R_2Si{=}O$-coordinated complex, (b) structures of silanone complexes **1a** and **2** reported by our group and (c) target complex **1b**.

complexes will provide us with information on applying silanone complexes as synthetic tools and materials.

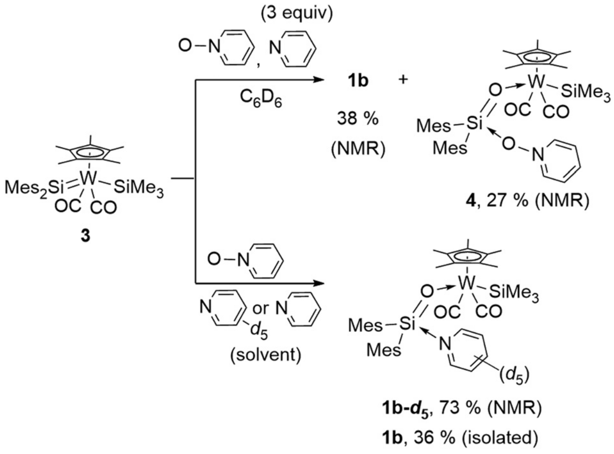
In comparison with silanones, silanone complexes **1a** and **2** have been found to be less reactive[8] as the silanone ligands are kinetically and thermodynamically stabilized by two bulky Mes substituents (Mes = 2,4,6-$Me_3C_6H_2$) and a Lewis base on the silicon atoms and coordination of the oxygen atoms to Lewis acidic transition metal fragments, respectively. Molybdenum complexes **2a** and **2b** gradually decomposed in C_6D_6 at 25 °C within 2 days.[8b] In contrast, tungsten complex **1a** was thermally stable and remained unchanged in C_6D_6 at 25 °C for at least 1 week.[8a] To evaluate the effect of the Lewis base on the reactivity of the silanone tungsten complex, we investigated the synthesis and reactions of the pyridine-stabilized silanone complex $Cp^*(OC)_2W\{O{=}SiMes_2(py)\}(SiMe_3)$ (**1b**, py = pyridine). Pyridine and 4-(dimethylamino)pyridine (DMAP) share a common steric size around the silanone silicon atom but pyridine (pK_b = 8.8) has a weaker Lewis basicity than DMAP (pK_b = 4.8). Thus pyridine-stabilized complex **1b** is expected to have a higher reactivity than DMAP-stabilized complex **1a**.

In this paper, we report the synthesis, structure and reactivity of pyridine-stabilized silanonetungsten complex **1b** and find that pyridine is more readily eliminated than DMAP from the Si atom, affording a more reactive silanone complex. It is also found that silanone complex **1b** is transformed *via* a similar reaction pathway proposed for a theoretically suggested silanethione ($R_2Si{=}S$, a heavier congener of silanone) complex intermediate $Cp(OC)_2W(S{=}SiPh_2)(SiH_3)$ (**A**, Cp = η^5-C_5H_5).[10]

Results and discussion

Synthesis and structure of a pyridine-stabilized silanonetungsten complex $Cp^*(OC)_2W\{O{=}SiMes_2(py)\}(SiMe_3)$ (1b)

As reported previously, silanone complex **1a** was synthesized by the oxygenation of the Si=W double bond in the silyl(silylene) complex $Cp^*(OC)_2W({=}SiMes_2)(SiMe_3)$ (**3**, Cp* = η^5-C_5Me_5) with pyridine-*N*-oxide (PNO) in the presence of DMAP.[8a,b] By following the synthetic method for **1a**, pyridine-stabilized complex **1b** was also obtained by the reaction of silyl(silylene) complex **3** with PNO in the presence of pyridine in C_6D_6, however, the yield was low (38% NMR yield, eqn (1)) and concomitantly a PNO-stabilized silanone complex $Cp^*(OC)_2W\{O{=}SiMes_2(PNO)\}(SiMe_3)$ (**4**)[8a] was formed (27% NMR yield). The yield of **1b** (**1b-*d*$_5$**) was significantly improved to 73% (NMR yield) when the reaction was performed in pyridine-d_5, and no **4** was detected at all. The reason for this improved yield could be the presence of excess amounts of pyridine, which facilitates the substitution of PNO in complex **4** and suppresses the elimination of pyridine from **1b**. Complex **1b** was isolated as brown crystals in 36% yield by the reaction of **3** with PNO in pyridine for 0.5 h (eqn (1)).



(1)

The characterization of **1b** was achieved by NMR and IR spectroscopy, elemental analysis, and X-ray crystal structure determination. The ^1H NMR spectrum showed signals for the Mes groups at 6.76, 2.29, and 2.07 ppm, the Cp* group at 1.91 ppm, and the $SiMe_3$ ligand at 0.93 ppm, which are identical to the chemical shifts observed for **1a**,[8a] along with the signals of the coordinated pyridine (8.32, 6.62, and 6.47 ppm). The ^{29}Si NMR spectrum showed two signals assignable to the $(py)Mes_2Si{=}O$ and $SiMe_3$ ligands at −21.1 and 19.1 ppm, respectively. The former chemical shift is comparable to that observed for the $(DMAP)Mes_2Si{=}O$ ligand in **1a** (−25.9 ppm)[8a] and within the range of those observed for both Lewis base (LB)- and Lewis acid (LA)-stabilized silanones $(LB)R_2Si{=}O(LA)$ (−14 to −76 ppm).[3b,g,4,7,8b] X-ray crystal structure determination of **1b** revealed that the unit cell contains two crystallographically independent molecules. Since the structural parameters of the two molecules are identical (see the ESI† for details), we discuss here the structure of **1b** using one of the two structural parameters. Complex **1b** exhibits a four-legged piano stool geometry with two COs, $SiMe_3$, and a Lewis base-stabilized silanone ligand $(py)Mes_2Si{=}O$ (Fig. 1). The interatomic distance between tungsten and silicon of the silanone ligand (3.629(2) Å) is significantly longer than those reported for the usual W–Si single bonds (2.55–2.65 Å)[8a,11] and the angle of W–O3–Si2 (154.91(15)°) is wider, indicating the η^1-cooridination mode of the silanone ligand. Similar structural features, *i.e.*, the four-legged piano stool geometry with a η^1-

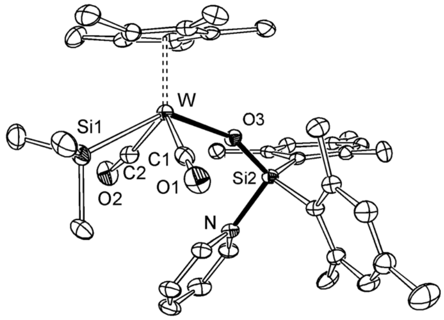
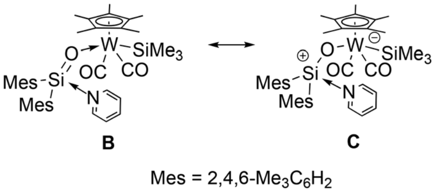


Fig. 1 ORTEP drawing of **1b**. H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): W–O3 2.154(2), O–Si2 1.561(2), W–Si1 2.6328(13), W–C1 1.956(4), W–C2 1.957(4); Si1–W–O3 137.42(7), C1–W–C2 107.54(13), W–O3–Si2 154.91(15).

silanone ligand, were observed in DMAP analogue **1a**.[8a] The W–O3 and Si2═O3 bond distances (2.154(2) and 1.561(2) Å, respectively) are comparable to those observed for complex **1a** (2.165(4) and 1.558(4) Å, respectively)[8a] and within the range of those observed for oxygen to tungsten coordination bonds (2.15–2.39 Å)[12] and Lewis base- and Lewis acid-stabilized silanones (LB)R_2Si═O(LA) (1.54–1.58 Å).[3b,4,7,8b] The nitrogen to silicon bond length (1.918(3) Å) is within the range of those observed for the usual nitrogen to silicon coordination bonds (1.83–1.94 Å),[8a,b,13] but intriguingly, is slightly longer (*ca.* 0.05 Å) than that of **1a** (1.865(5) Å).[8a] This elongation implies the weaker coordination of pyridine compared to that of DMAP.

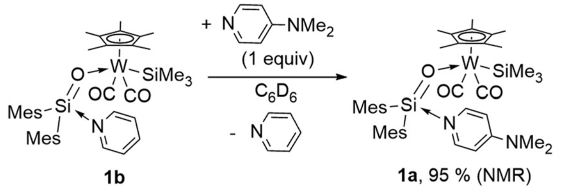
In the IR spectrum of **1b**, intense absorptions of *ν*COs were observed at 1857 and 1768 cm^{-1}, whose frequencies are identical to those observed for complex **1a** (1857 and 1763 cm^{-1}).[8a] This indicates that the electron density on the tungsten center in **1b** is almost identical to that in **1a**. Thus, the electron-donating abilities of the two silanone ligands (L)Mes_2Si═O (L = DMAP and py) are identical, although the Lewis basicity of py is weaker than that of DMAP. Furthermore, it should be noted that the absorption of *ν*COs in **1b** is comparable to that observed for an anionic complex with similar geometry $[Cp^*(OC)_2WH_2]^-$ (1862 and 1752 cm^{-1}).[14] Based on the results obtained from both X-ray crystal structure determination and IR spectroscopy, the structure of **1b** can be depicted as a resonance form shown in Scheme 3 and both canonical forms **B** and **C** significantly contribute to the structure of complex **1b**.



Scheme 3 The structures of two canonical forms **B** and **C** for silanone complex **1b**.

Reaction of $Cp^*(OC)_2W\{O═SiMes_2(py)\}(SiMe_3)$ (1b) with DMAP

As discussed above, the Si–N bond length in pyridine-stabilized complex **1b** is longer than that in DMAP analogue **1a**. This result suggests that the coordination of pyridine is weaker than that of DMAP. Actually, the reaction of **1b** with 1 equiv. of DMAP immediately proceeded *via* the substitution of pyridine with DMAP to form complex **1a** in 95% NMR yield (eqn (2)). This result clearly demonstrated the strong coordination of DMAP in comparison with that of pyridine.

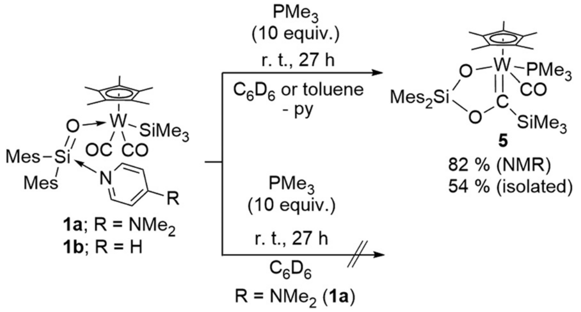


(2)

Thermal reactions of $Cp^*(OC)_2W\{O═SiMes_2(L)\}(SiMe_3)$ (L = DMAP (1a), py (1b)) in the absence and presence of PMe_3

DMAP-stabilized complex **1a** is thermally stable and remained unchanged in C_6D_6 at 25 °C for at least 1 week.[8a] In contrast to **1a**, pyridine-stabilized complex **1b** decomposed in C_6D_6 at r. t. within 24 h to give a complex mixture of unidentified products. The decomposition of **1b** was suppressed in the presence of excess pyridine-d_5 (as a solvent) and as a result 70% of **1b** remained unchanged after 1 week.

The reaction of **1b** with excess (10 equiv.) PMe_3 in C_6D_6 at r. t. for 27 h gave a five-membered W═C–O–Si–O metallacyclic carbene complex, $Cp^*(OC)W(═C(SiMe_3)OSiMe_2O)(PMe_3)$ (**5**) in 82% NMR yield *via* the elimination of pyridine (eqn (3)). Complex **5** was isolated as brown crystals in 54% yield by the reaction of **1b** with PMe_3 in toluene. In contrast, no reaction occurred between **1a** and PMe_3 under similar reaction conditions. The difference in the reactivity between **1b** and **1a** could be due to the coordination strength between pyridine and DMAP to the silicon center; pyridine dissociates from the silicon atom but DMAP does not dissociate even in the presence of PMe_3.



(3)

X-ray crystal structure determination (Fig. 2) revealed that complex **5** possesses a five-membered W═C–O–Si–O metallacyclic structure with PMe_3, CO and Cp* ligands on the tungsten center. The bond distance between W and C2 (2.027(6) Å) is comparable to those observed for the usual W═C double bonds found in 5-membered metallacyclic structures

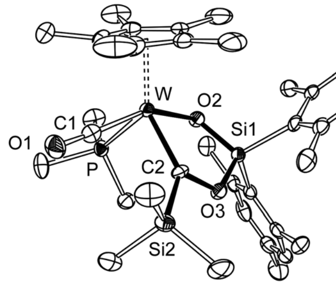
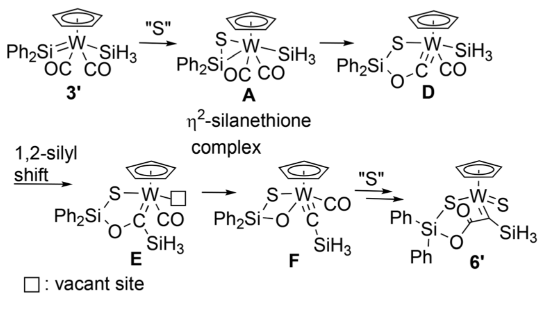


Fig. 2 ORTEP drawing of **5**. H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): W–C2 2.027(6), W–P 2.4717(15), W–O2 2.131(4), Si1–O2 1.602(4), Si1–O3 1.664(4), W–C1 1.975(7); P–W–C2 95.53(17), P–W–O2 78.23(11), W–O2–Si1 116.2(2), W–C2–Si2 133.4(3), W–C2–O3 120.6(4), Si2–C2–O3 105.6(3).

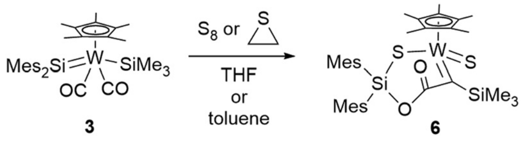
(1.97–2.18 Å).[15] The sum of the bond angles around C2 is *ca.* 360°, indicating the sp^2 hybridization of the C2 center. The ^{13}C NMR spectrum showed a doublet resonance at a significant downfield (313.6 ppm, $^2J_{C-P}$ = 8.3 Hz). This chemical shift is within the usual range of those observed for metallacyclic carbene tungsten complexes (254–343 ppm).[15] These data clearly demonstrated that complex **7** bears the W═C2 double bond. The W–P bond distance (2.4717(15) Å) is within the range of those observed for the usual phosphine to tungsten coordination bonds (2.42–2.56 Å).[15d,16] The ^{31}P NMR spectrum showed a singlet signal assignable to the PMe$_3$ ligand at −22.2 ppm, which is within the chemical shift range of those reported for PMe$_3$-coordinated tungsten complexes (−4 to −33 ppm).[15d,16] The W–O2 (2.131(4) Å) and Si–O (Si1–O2: 1.602(4), Si1–O3: 1.664(4) Å) bond distances are comparable to those observed for the usual W–OSiR$_3$ (1.79–2.10 Å)[8a,17] and Si–O (1.60–1.66 Å)[18] single bonds, respectively.

Thermal transformation of Cp*(OC)W(═C(SiMe$_3$)OSiMes$_2$O)(PMe$_3$) (5)

We have already reported that the reaction of the silyl(silylene) tungsten complex Cp*(OC)$_2$W(═SiMes$_2$)(SiMe$_3$) (**3**) with a sulfuration reagent, instead of an oxygenation reagent, afforded six-membered cyclic carbene complex **6** (eqn (4)).[10a] A plausible formation mechanism of **6′** (model complex of **6**) proposed theoretically using complex **3′** (Scheme 4)[10b] revealed that complex **3′** is initially transformed to silanethione-coordinated complex **A** *via* sulfur-addition to the Si═W bond, and the subsequent W–Si bond cleavage and Si–O bond formation between the silanethione and carbonyl ligands gives 5-membered W≡C–O–Si–S metallacyclic carbyne complex **D**. The 1,2-silyl shift from the tungsten to the carbyne carbon leads to the formation of 16e five-membered W═C–O–Si–S metallacyclic carbene complex **E**. The C–O bond cleavage in the metallacycle of complex **E** and the W–O bond formation afford carbyne complex **F**, which is converted to complex **6′** in the presence of a sulfuration reagent *via* several steps. It should be noted that the structure of complex **5** is comparable to that of the PMe$_3$-adduct of complex **E**, as both complexes include similar five-membered W═C(SiR$_3$)–O–Si–E metallacyclic skeletons (E = O and S). Since complex **E** is proposed to be converted into a four-membered W–O–Si–S metallacycle with a carbyne ligand, **F**, as shown in Scheme 4, complex **5** is expected to transform into a complex bearing a structure similar to that of **F**. To evaluate the similarity in the reactivity between the W═C(SiR$_3$)–O–Si–O and W═C(SiR$_3$)–O–Si–S metallacyclic carbene complexes, further transformation of complex **5** was investigated.

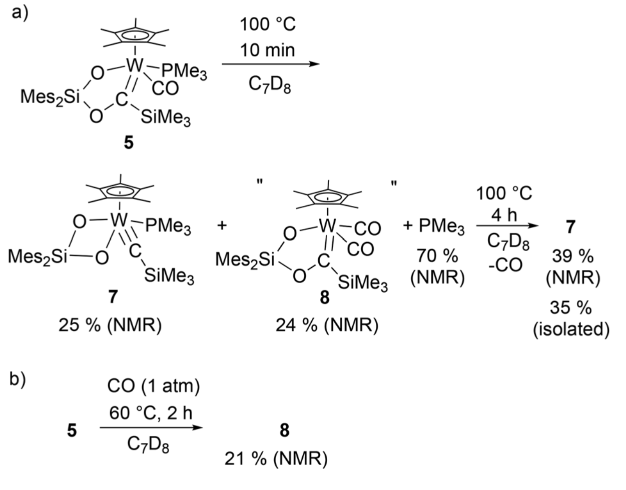


Scheme 4 A plausible formation mechanism of **6′** theoretically proposed using complex **3′**.[10b]



(4)

Heating of the C$_7$D$_8$ solution of **5** at an elevated temperature (100 °C) for 10 min resulted in the complete consumption of **5** and formation of a mixture of a four-membered W–O–Si–O metallacyclic complex with carbyne and PMe$_3$ ligands Cp*W(OSiMes$_2$O)(≡CSiMe$_3$)(PMe$_3$) (**7**) and **8** in 25 and 24% NMR yields, respectively, along with free PMe$_3$ in 70% NMR yield (Scheme 5a, the sums of the NMR yields of the tungsten fragment and PMe$_3$ are 49 (**7**+**8**) and 95% (**7** + free PMe$_3$), respectively). When the resultant mixture was further heated at



Scheme 5 (a) Thermal transformation of **5** in C$_7$D$_8$ at 100 °C. (b) Reaction of **5** with 1atm CO in C$_7$D$_8$ at 60 °C.

100 °C, complex **8** was gradually converted to complex **7** and completely consumed after 4 h. During the heating process, the yield of **7** increased and finally reached 39%. Complex **8** was also formed by the reaction of **5** with 1 atm CO in C_7D_8 at 60 °C for 2 h (Scheme 5b). At this moment, the isolation of complex **8** had not been accomplished yet,[19] but based on the ^{1}H NMR and IR data,[20] the structure of **8** was deduced to be a five-membered metallacyclic carbene complex with two CO ligands $Cp^*(OC)_2W\{{=}C(SiMe_3)OSiMes_2O\}$.

Complex **7** was isolated as yellow crystals in 35% yield by the reaction of **5** in toluene at 100 °C. As described below, the structure of complex **7** shows a four-membered W–O–Si–O metallacyclic skeleton with carbyne and PMe_3 (L type) ligands. To the best of our knowledge, only one organotransition metal complex with a chelating R_2SiO_2 ligand has been known.[21] The structural features of complex **7** are comparable to those of complex **F**, *i.e.*, the 4-membered W–O–Si–S metallacyclic skeleton with carbyne and CO (L type) ligands. Several trials for the transformations of complexes **5** and **7** to the oxygen analogue of **6** in the presence of an oxygenation reagent, PNO, (in the absence and presence of 1 atm CO) have been unsuccessful so far, although complex **F** is proposed to be converted into complex **6′** in the presence of a sulfuration reagent. Heating of the silanone complex **1b** in C_7D_8 at 100 °C for 4 h in the presence of excess PMe_3 gave a complex mixture of unidentified products and no complex **7** was detected at all.

X-ray crystal structure determination (Fig. 3) revealed that complex **7** shows a four-legged piano stool geometry with a four-membered cyclic W–O–Si–O skeleton, carbyne and PMe_3 ligands. The W–C1–Si1 bond angle (176.5(2)°) is almost linear, indicating the sp-hybridization of the C1 atom. The bond distance between the tungsten and C1 atom (1.802(3) Å) is within the range of those observed for the usual $W{\equiv}C{-}SiMe_3$ triple bonds (1.73–1.82 Å).[22] The ^{13}C NMR spectrum showed a doublet signal at a significant downfield (343.7 ppm, $^2J_{C-P}$ = 21.4 Hz). The chemical shift and coupling constant are comparable to those observed for the usual carbyne(phosphine) tungsten complexes (285–359 ppm, $^2J_{C-P}$ = 8–15 Hz).[23] These data clearly demonstrated that complex **7** bears the W≡C1 triple bond. The W–P bond distance (2.4898(9) Å) is within the range of those observed for the usual W–P coordination bonds (2.42–2.56 Å).[15d,16] The ^{31}P NMR spectrum showed a singlet signal assignable to the PMe_3 ligand at −16.4 ppm along with a ^{183}W satellite signal (^1J (^{31}P–^{183}W) = 210 Hz), whose chemical shift and coupling constant are comparable to those reported for the usual W–PMe_3 complexes (−4 to −33 ppm, and ^1J (^{31}P–^{183}W) = 232–482 Hz, respectively).[15d,16]

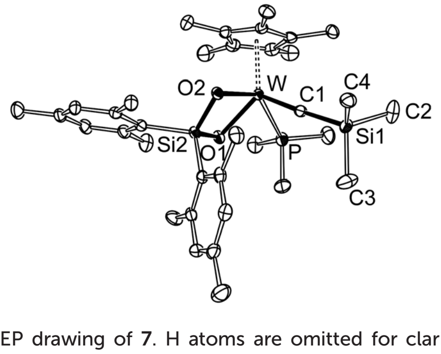
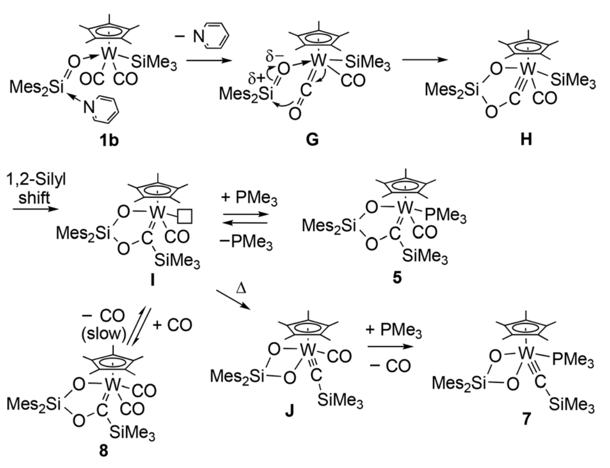


Fig. 3 ORTEP drawing of **7**. H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): W–C1 1.802(3), W–P 2.4898(9), W–O1 2.097(2), W–O2 2.056(2), Si2–O1 1.630(2), Si2–O2 1.637(2); W–C1–Si1 176.5(2), P–W–C1 81.57(10), O1–W–C1 113.30(12), O2–W–C1 100.27 (12).

A plausible formation mechanism of complexes 5 and 7

As described above, silanone complex **1b** was converted to five-membered metallacyclic carbene complex **5** in the presence of PMe_3 and complex **5** was transformed to four-membered W–O–Si–O metallacyclic complex **7**. The structural similarities between complexes **5** and **E** and complexes **7** and **F** imply that silanone complex **1b** and silanethione complex **A** are transformed *via* a similar reaction pathway, *i.e.*, Si–O bond formation between the $R_2Si{=}E$ and CO ligands, 1,2-silyl shift, C–O bond cleavage in the metallacycle, and W–O bond formation. Therefore, based on both the reaction similarity and reaction mechanism theoretically proposed for the formation of complex **6′** (Scheme 4), a plausible formation mechanism of complexes **5** and **7** is deduced as shown in Scheme 6. The elimination of pyridine from the silanone ligand in complex **1b** affords base-free silanone complex **G**. The intramolecular Si–O bond formation between the Si atom of the silanone ligand and an oxygen atom in the CO ligand affords metallacyclic carbyne complex **H**. The 1,2-silyl shift from the tungsten to the carbyne carbon leads to the formation of 16*e* complex **I**, which is converted to complex **5** *via* the coordination of PMe_3 to the tungsten center. The transformation of **5** initially takes place *via* the elimination of PMe_3 to give 16*e* complex **I**. The C–O bond fission in the metallacycle of complex **I** and the subsequent O–W bond formation affords carbyne complex **J**. The substitution of CO with PMe_3 yields complex **7**. In the presence of CO (free CO would be formed along with the generation of complex **7**), complex **I** is trapped by CO to form complex **8**, which is con-



Scheme 6 A plausible formation mechanism of complexes **5** and **7**.

verted to complex **I** again, but slowly, by the release of the CO ligand under the reaction conditions.

Conclusions

In summary, we have reported the synthesis, structure, and reactivity of pyridine-stabilized silanonetungsten complex **1b** and enhanced the reactivity of a silanone-coordinated transition metal complex. The reaction of complex **1b** with DMAP proceeds *via* substitution of pyridine with DMAP to give DMAP-stabilized silanone complex **1a**. In contrast, the reaction of **1b** with PMe_3 proceeds *via* elimination of pyridine and Si–O bond formation to afford complex **5**, and no PMe_3-stabilized silanone complex $Cp^*(OC)_2W\{O{=}SiMes_2(PMe_3)\}(SiMe_3)$ was obtained. The difference in the reactivity between DMAP and PMe_3 with complex **1b** would be their coordination strength to the Si atom in the silanone ligand; the strong coordination of DMAP hampers the intramolecular Si–O bond formation between silanone and CO ligands. A similarity in the reactivity between the silanone complex and silanethione complex was observed in both experimental and theoretical investigations. Thus, in the transformations of **1b** and **A** to **5** and **E**, respectively, the silanone and silanethione ligands are incorporated into the identical cyclic W=C–O–Si–E (E = O, S) structure while maintaining the W–E bonds. These results indicate the strong coordination of the $R_2Si{=}E$ ligands to the tungsten fragment $Cp^*(OC)_2W(SiMe_3)$.

Experimental

General procedures

All manipulations were performed using either standard Schlenk tube techniques under nitrogen, vacuum line techniques, or a dry box under nitrogen. $Cp^*(OC)_2W({=}SiMes_2)(SiMe_3)$ (**3**) was prepared according to the published procedure.[11d] The other chemicals were purchased from Wako Pure Chemical Industries (toluene, Et_2O, hexane, C_5D_5N, C_6D_6, C_7D_8, and CH_2Cl_2) and Kanto Chemical (pyridine and CD_2Cl_2) and Aldrich (PMe_3) or TCI (pyridine-*N*-oxide (PNO)) and purified as follows. Hexane, toluene and Et_2O were dried by refluxing over sodium benzophenone ketyl followed by distillation under a nitrogen atmosphere before use. Pyridine-*N*-oxide (PNO) was recrystallized from Et_2O before use. C_6D_6 and C_7D_8 were dried over molecular sieves 4 A, and degassed over a potassium mirror followed by distillation *in vacuo* before use. Pyridine, C_5D_5N, and CD_2Cl_2 were dried over molecular sieves 4 A, and degassed by freeze–pump–throw cycling.

NMR spectra were recorded on a JNM-ECS300, a JNM-ECS400, or a JNM-ECS600 Fourier transform spectrometer at room temperature. Chemical shifts are reported in ppm with respect to residual internal C_6D_5H (δ 7.16) or $C_6D_5CD_2H$ (δ 2.08) for ^1H NMR, C_6D_6 (δ 128.1), C_5D_5N (δ 123.8) or CD_2Cl_2 (δ 54.0) for ^{13}C NMR, external 85% H_3PO_4 aq. (δ 0.0) for ^{31}P NMR and $SiMe_4$ (δ 0.0) for ^{29}Si NMR. IR spectra were recorded on an Agilent Cary 630 FTIR spectrometer at room temperature. Elemental analyses were performed at the Microanalytical Center, Gunma University or Prof. Sunada's Laboratory at the Institute of Industrial Science, The University of Tokyo.

Isolation of $Cp^*(OC)_2W\{O{=}SiMes_2(py)\}(SiMe_3)$ (1b). To a pyridine solution (9 mL) of $Cp^*(OC)_2W({=}SiMes_2)(SiMe_3)$ (**3**, 75 mg, 1.0×10^{-4} mol) was added PNO (9.8 mg, 1.0×10^{-4} mol) at r. t. The reaction mixture was stirred at r. t. for 20 min. The solution was concentrated to dryness *in vacuo*, and the residue was washed with hexane (2 mL × 3) to give brown solids. The residual brown solids were dissolved in toluene (7 mL) and the solution was filtered through a glass filter. To the filtrate were added hexane (12 mL) and pyridine (0.2 mL), and it was cooled to −35 °C to afford brown crystals of $Cp^*(OC)_2W\{O{=}SiMes_2(py)\}(SiMe_3)$ (**1b**) in 35% yield (29 mg, 3.6×10^{-5} mol). ^1H NMR (400 MHz, C_6D_6) δ/ppm 8.30–8.34 (m, 2H, 2,6-H, py), 6.76 (s, 4H, *m*-H, Mes), 6.60–6.64 (m, 1H, 4-H, py), 6.45–6.48 (m, 2H, 3,5-H, py), 2.29 (s, 12H, *o*-Me), 2.07 (s, 6H, *p*-Me), 1.91 (s, 15H, C_5Me_5), 0.93 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (150.9 MHz, C_5D_5N) δ/ppm 246.8 ($^1J_{W-C}$ = 186 Hz, CO), 149.7 (2,6-py), 145.1 (Mes), 140.2 (Mes), 135.5 (4-py), 132.7 (Mes), 130.0 (Mes), 123.3 (3,5-py), 102.0 (C_5Me_5), 24.7 (*o*-Me), 20.8 (*p*-Me), 11.5 ($C_5\mathit{Me}_5$), 6.9 ($SiMe_3$). $^{29}Si\{^1H\}$ NMR (119.2 MHz, C_6D_6) δ/ppm 19.1 ($SiMe_3$), −21.1 ($SiMes_2$). IR (C_6D_6) νCO 1857 (s), 1768 (s) cm^{-1}. Anal. calcd for **1b** $C_{38}H_{51}NO_3Si_2W$: C, 56.36; H, 6.35; N, 1.73. Found: C, 56.27; H, 6.59; N, 1.83.

Isolation of $Cp^*(OC)W({=}C(SiMe_3)OSiMes_2O)(PMe_3)$ (5). To a toluene solution (20 mL) of $Cp^*(OC)_2W\{O{=}SiMes_2(py)\}(SiMe_3)$ (**1b**, 413 mg, 5.10×10^{-4} mol) was added PMe_3 (520 µL, 5.11×10^{-3} mol) at r. t. The reaction mixture was stirred at r. t. for 27 h. The solution was concentrated to *ca.* 2 mL *in vacuo*. To the solution was added hexane (8 mL) and the resulting solution was cooled to −35 °C to give brown crystals of $Cp^*(OC)W({=}C(SiMe_3)OSiMes_2O)(PMe_3)$ (**5**) in 54% yield (223 mg, 2.76×10^{-4} mol). ^1H NMR (400 MHz, C_6D_6) δ/ppm 6.80 (s, 2H, *m*-H), 6.78 (s, 2H, *m*-H), 2.90 (s, 6H, *o*-Me), 2.72 (s, 6H, *o*-Me), 2.14 (s, 6H, *p*-Me), 1.59 (s, 15H, C_5Me_5), 1.00 (d, $^2J_{H-P}$ = 8.8 Hz, 9H, PMe_3), 0.55 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (150.9 MHz, CD_2Cl_2) δ/ppm 313.6 (d, $^2J_{C-P}$ = 8.3 Hz, $^1J_{C-W}$ = 119 Hz, W=C), 259.7 (d, $^2J_{C-P}$ = 10.4 Hz, $^1J_{C-W}$ = 146 Hz, CO), 144.1 (Mes), 137.8 (Mes), 136.9 (Mes), 134.9 (Mes), 129.0 (Mes), 128.4 (Mes), 128.3 (Mes), 125.3 (Mes), 101.7 (C_5Me_5), 24.5 (*o*-Me), 23.5 (*o*-Me), 20.8 (*p*-Me), 20.7 (*p*-Me), 16.5 (d, $^1J_{C-P}$ = 29.1 Hz, PMe_3), 11.3 ($C_5\mathit{Me}_5$), 1.08 ($SiMe_3$). $^{29}Si\{^1H\}$ NMR (119.2 MHz, C_6D_6) δ/ppm 0.71 ($SiMe_3$), −21.8 ($SiMes_2$). $^{31}P\{^1H\}$ NMR (242.9 MHz, C_6D_6) δ/ppm −22.2 (s, $^1J_{P-W}$ = 318 Hz). IR (C_6D_6) νCO 1870 (s), νSi–O 985 (s) cm^{-1}. Anal. calcd for **5** $C_{36}H_{55}O_3PSi_2W$: C, 53.59; H, 6.87. Found: C, 53.40; H, 6.91.

Isolation of $Cp^*W(OSiMes_2O)({\equiv}CSiMe_3)(PMe_3)$ (7). A toluene solution (10 mL) of $Cp^*(OC)W({=}C(SiMe_3)OSiMes_2O)(PMe_3)$ (**5**, 185 mg, 2.29×10^{-4} mol) was stirred at 100 °C for 4 h. The solution was concentrated to *ca.* 1 mL *in vacuo*. To the solution was added hexane (5 mL) and it was cooled to −35 °C to give brown crystals of $Cp^*W(OSiMes_2O)({\equiv}CSiMe_3)(PMe_3)$ (**7**) in 32% yield (58 mg, 7.2×10^{-5} mol). ^1H NMR (400 MHz, C_6D_6) δ/ppm 6.93 (s, 2H, *m*-H), 6.72 (s, 2H, *m*-H), 3.32 (s, 3H, *o*-Me), 2.94 (s, 3H, *o*-Me), 2.84 (s, 3H, *o*-Me), 2.61 (s, 3H, *o*-Me), 2.19 (s, 3H, *p*-Me), 2.14 (s, 3H, *p*-Me), 1.83 (s, 15H, C_5Me_5), 1.28 (d, $^2J_{H-P}$ = 9.6 Hz, 9H, PMe_3), 0.13 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (150.9 MHz, C_6D_6) δ/ppm 343.7 (d, $^2J_{C-P}$ = 21.4 Hz, W═C), 144.0 (Mes), 143.0 (Mes), 138.0 (Mes), 137.4 (Mes), 137.3 (Mes), 135.9 (Mes), 129.0 (Mes), 128.3 (Mes), 113.7 (C_5Me$_5$), 22.6–23.1 (*p*-Me, *o*-Me), 21.0 (d, $^1J_{C-P}$ = 4.4 Hz, PMe_3), 11.8 (C_5*Me*$_5$), 2.97 ($SiMe_3$). $^{29}Si\{^1H\}$ NMR (119.2 MHz, C_7D_8) δ/ppm −8.7 (d, $^3J_{Si-P}$ = 32.8 Hz, $SiMe_3$), −18.4 (d, $^3J_{Si-P}$ = 3.7 Hz, $SiMes_2$). $^{31}P\{^1H\}$ NMR (242.9 MHz, C_6D_6) δ/ppm −16.4 (s, $^1J_{P-W}$ = 210 Hz). IR (C_6D_6) νSi–O 1147 (s) cm^{-1}. Anal. calcd for **7** $C_{35}H_{55}O_2PSi_2W$: C, 53.98; H, 7.12. Found: C, 53.67; H, 6.95.

Reaction of 5 with 1 atm of CO in C_7D_8. A C_7D_8 solution (0.5 mL) of Cp*(OC)W(═C($SiMe_3$)O$SiMes_2$O)(PMe_3) (**5**, 6.8 mg, 8.4×10^{-6} mol) in a Pyrex NMR tube (5 mm o.d.) equipped with a Teflon stop valve was degassed by freeze–pump–throw cycling. After three cycles, the solution was charged with 1 atm CO. The resulting mixture was heated at 60 °C for 2 h and the reaction was periodically monitored by ^1H NMR spectroscopy.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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19 Based on the plausible formation mechanism in Scheme 5, we tried to synthesize complex **8** by the reaction of complex **1b** with 1 atm CO in C_6D_6 or C_7D_8 at r. t. However, several unidentified compounds were formed and complex **8** was not observed.

20 ^{1}H NMR (400 MHz, C_7D_8) δ/ppm 6.61 (s, 2H, *m*-H), 6.59 (s, 2H, *m*-H), 2.78 (s, 3H, *o*-Me), 2.57 (s, 3H, *o*-Me), 2.50 (s, 3H, *o*-Me), 2.39 (s, 3H, *o*-Me), 2.05 (s, 3H, *p*-Me), 2.00 (s, 3H, *p*-Me), 1.69 (s, 15H, C_5Me_5), 0.19 (s, 9H, $SiMe_3$). IR (C_7D_8) νCO 1945, 1870 (s) cm^{-1}.

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