# Synthesis and Characterization of DMAP-Stabilized Aryl(silylene) Complexes and (Arylsilyl)(DMAP) Complexes of Tungsten: Mechanistic Study on the Interconversion between These Complexes via 1,2-Aryl Migration

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Photoreaction of a mixture of $Cp^*(CO)_3WMe$ ($Cp^* = \eta^5$-$C_5Me_5$) and $HSiR_2Ar$ [$R_2Ar = Me_2Ph$, $Me_2(p$-Tol), $Me(p$-$Tol)_2$, and $(p$-$Tol)_3$] in the presence of 4-(dimethylamino)pyridine (DMAP) gave DMAP-stabilized aryl(silylene) complexes $Cp^*(CO)_2W(Ar)(=SiR_2 \cdot DMAP)$ [**1a**, R = Me, Ar = Ph; **1b**, R = Me, Ar = *p*-Tol; **1c**, $R_2$ = Me(*p*-Tol), Ar = *p*-Tol; **1d**, R = Ar = *p*-Tol] via 1,2-migration of the aryl group from a silyl ligand to a tungsten center. Thermal reactions of $Cp^*(CO)_2W(DMAP)Me$ (**2**) with $HSiR_2Ar$ at room temperature also gave **1a**−**d**, and in all cases the yields were higher than those in the photoreaction. Silylene complexes **1a**−**d** easily isomerized to arylsilyl complexes $Cp^*(CO)_2W(DMAP)(SiR_2Ar)$ [**3a**, R = Me, Ar = Ph; **3b**, R = Me, Ar = *p*-Tol; **3c**, $R_2$ = Me(*p*-Tol), Ar = *p*-Tol; **3d**, R = Ar = *p*-Tol] at 40−55 °C. On the other hand, irradiation of arylsilyl complexes **3a**−**d** reproduced silylene complexes **1a**−**d**, implying that the 1,2-aryl-migration between tungsten and silicon is reversible. The molecular structures of **1c**, **2**, **3a**, and **3d** were determined by X-ray crystallography. A kinetic study on the 1,2-aryl-migration in the thermal isomerization from **1a**−**d** to **3a**−**d** suggests that the rate-determining step involves dissociation of DMAP from **1a**−**d**.

## Introduction

Transition-metal silylene complexes are proposed as key intermediates for metal-mediated scrambling of the substituents of silanes, dehydrogenative coupling of silanes, etc.[1] In these transformation reactions, silylene complexes are generally formed through silyl complexes generated from metal complexes and hydrosilanes, and these processes are mostly reversible. The interconversion between the silylene complexes and silyl complexes is supposed to proceed via 1,2-migration of a substituent R′ as shown in Scheme 1. Although there are many reports on the 1,2-migration of a hydrogen[2] or a silyl group[3] on a silyl ligand giving silylene complexes, those on 1,2-migration of a hydrocarbyl[4−7] group have been rare.

The 1,2-migration of hydrocarbyl groups between transition metal and silicon atoms is interesting because of its relationship with Si−C bond cleavage/formation reactions mediated by metal−silicon complexes.[8] However, the experimental investigations on the 1,2-migration have been limited to several late transition-metal complexes: Bergman et al. reported alkyl- and aryl-migration reactions between cationic iridium-silyl and -silylene complexes.[4] 1,2-Migration reactions of an alkyl or an aryl group on a metal center to a silylene ligand have also been proposed in several reactions of iridium[1a,9] and platinum[10] complexes. On the other hand, we have recently reported on the irreversible 1,2-migration of an aryl group in an early transition-metal silyl complex where the *Si*,*N*-chelated tungsten complex $Cp^*(CO)_2W\{\kappa^2(Si,N)$-$Me_2N(o$-$C_6H_4SiMe_2)\}$ is thermally unstable and is converted to the base-stabilized aryl(silylene) complex $Cp^*(CO)_2W\{\kappa^2(Si,C)$-$SiMe_2NMe_2(o$-$C_6H_4)\}$ at room temperature.[6] Because of the lability of the amine ligand, the *Si*,*N*-chelate complex can easily generate a 16-electron silyl complex that is a crucial intermediate for the 1,2-aryl-migration. As a closely related example, Sakaba et al. recently observed the 1,2-migration of an alkynyl group in the

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(1) (a) Okazaki, M.; Tobita, H.; Ogino, H. *Dalton Trans.* **2003**, 493, and references therein. (b) Ogino, H. *Chem. Rec.* **2002**, *2*, 291.
(2) (a) Sakaba, H.; Tsukamoto, M.; Hirata, T.; Kabuto, C.; Horino, H. *J. Am. Chem. Soc.* **2000**, *122*, 11511. (b) Watanabe, T.; Hashimoto, H.; Tobita, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 218. (c) Ochiai, M.; Hashimoto, H.; Tobita, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 8192. (d) Waterman, R.; Hayes, P. G.; Tilley, T. D. *Acc. Chem. Res.* **2007**, *40*, 712.
(3) (a) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. (b) Ueno, K.; Asami, S.; Watanabe, N.; Ogino, H. *Organometallics* **2002**, *21*, 1326. (c) Tobita, H.; Matsuda, A.; Hashimoto, H.; Ueno, K.; Ogino, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 221. (d) Hirotsu, M.; Nunokawa, T.; Ueno, K. *Organometallics* **2006**, *25*, 1554. (e) Ueno, K.; Masuko, A.; Ogino, H. *Organometallics* **1997**, *16*, 5023. (f) Ueno, K.; Sakai, M.; Ogino, H. *Organometallics* **1998**, *17*, 2138. (g) Tobita, H.; Kurita, H.; Ogino, H. *Organometallics* **1998**, *17*, 2844.
(4) (a) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462. (b) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 1816. (c) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *Organometallics* **2001**, *20*, 3220. (d) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *Organometallics* **2002**, *21*, 4648.
(5) (a) Sakaba, H.; Yoshida, M.; Kabuto, C.; Kabuto, K. *J. Am. Chem. Soc.* **2005**, *127*, 7276. (b) Mausumi, R.; Yoshihide, N.; Sato, H.; Sakaba, H.; Sakaki, S. *J. Am. Chem. Soc.* **2006**, *128*, 11927.
(6) Okazaki, M.; Suzuki, E.; Miyajima, N.; Tobita, H.; Ogino, H. *Organometallics* **2003**, *22*, 4633.
(7) Begum, R.; Komuro, T.; Tobita, H. *Chem. Lett.* **2007**, 650.
(8) Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 419.
(9) Okazaki, M.; Tobita, H.; Ogino, H. *J. Chem. Soc., Dalton Trans.* **1997**, 3531.
(10) Ozawa, F.; Kitaguchi, M.; Katayama, H. *Chem. Lett.* **1999**, 1289.

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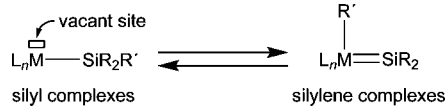
**Scheme 1. 1,2-Migration of the Substituent R′ in the Conversion between Silyl Complexes and Silylene Complexes**

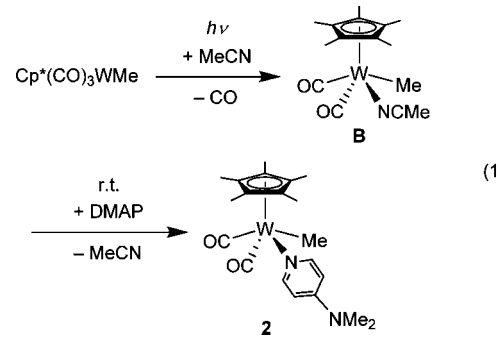



intermediary alkynylsilyl tungsten complexes giving alkynyl-bridged W–Si complexes.[5]

Here we report the synthesis of aryl(silylene) tungsten complexes via 1,2-aryl-migration from 16-electron silyl complexes in the presence of an external base, 4-(dimethylamino)pyridine (DMAP). DMAP is commonly used as a base to stabilize silylene complexes by its coordination to the Lewis acidic silylene silicon atom,[11] which can facilitate the formation of the silylene complexes. To generate the 16-electron silyl complexes, we employed two routes: (1) photoreaction of $Cp^*(CO)_3WMe$ with tertiary arylsilanes and (2) thermal reaction of $Cp^*(CO)_2W(DMAP)Me$ (**2**) with tertiary arylsilanes. In route 1, the photoinduced dissociation of a CO ligand in $Cp^*(CO)_3WMe$ generates 16e methyl complex $Cp^*(CO)_2WMe$ that can react with hydrosilanes $HSiR_3$ to give 16e silyl tungsten complexes $Cp^*(CO)_2W(SiR_3)$ via Si–H oxidative addition of silanes and methane elimination. In relation to route 2, Sakaba et al. previously reported that the thermally labile pyridine complex $Cp^*(CO)_2W(py)Me$ (**A**, py = pyridine) is versatile for the synthesis of pyridine-stabilized hydrido(silylene) complexes $Cp^*(CO)_2W(H)(=SiR_2\cdot py)$ ($R_2$ = $Ph_2$, MePh, $Et_2$) by the reaction with secondary silanes. This reaction proceeds via 1,2-H migration on the 16e silyl complexes $Cp^*(CO)_2W(SiHR_2)$ ($R_2$ = $Ph_2$, MePh, $Et_2$) generated as intermediates.[2a] In route 2 of our reaction, complex **2**, the DMAP analogue of complex **A**, acts as a good precursor of DMAP-stabilized silylene complexes, and the stronger Lewis basicity of DMAP compared to that of pyridine resulted in the cleavage of more robust silicon−carbon bonds. A part of this work has been published as a preliminary report.[12]

## Results and Discussion

**Synthesis of $Cp^*(CO)_2W(DMAP)Me$ (2).** A methyl tungsten complex having a DMAP ligand $Cp^*(CO)_2W(DMAP)Me$ (**2**), an important precursor of silylene complexes in this research, was synthesized according to a method analogous to that for the synthesis of pyridine complex $Cp^*(CO)_2W(py)Me$ (**A**).[2a] Thus, irradiation of $Cp^*(CO)_3WMe$ in MeCN with a 450 W medium-pressure Hg lamp ($\lambda > 300$ nm) led to the dissociation of a CO ligand followed by coordination of MeCN to give $Cp^*(CO)_2W(NCMe)Me$ (**B**).[2a,5,6,13] Then the substitution of the labile MeCN ligand in **B** with a DMAP molecule at room temperature in toluene gave the DMAP complex **2** in 86% yield (eq 1). Complex **2** was characterized by spectroscopy and elemental analysis. The molecular structure of **2** having a four-legged piano-stool geometry was confirmed by X-ray crystal structure analysis (Figure 1, Table 1). The DMAP ligand and the methyl ligand were located at mutually *cis* positions on the tungsten center. This geometry is consistent with the observation of two inequivalent signals (250.8, 266.2 ppm) assignable to the CO ligands in the $^{13}C\{^1H\}$ NMR spectrum of **2**.




(1)

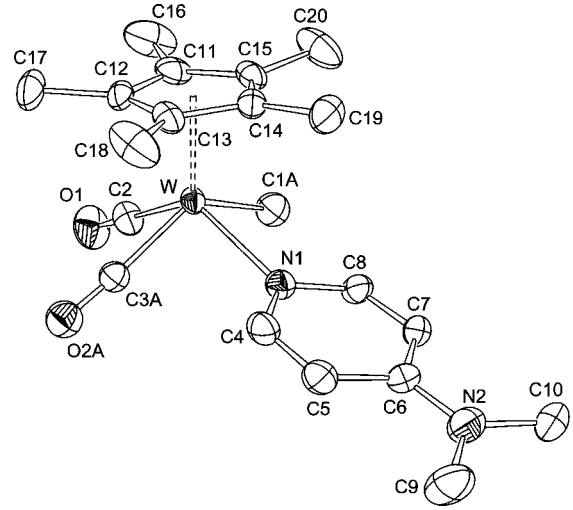



**Figure 1.** ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity. The sites of the methyl ligand and the carbonyl ligand are mutually disordered with the occupancy factors 61:39. Each one of the disordered atoms with the higher occupancy factors (O2A, C1A, and C3A) is depicted.

**Table 1. Selected Bond Distances (Å) and Angles (deg) in $Cp^*(CO)_2W(DMAP)Me$ (2)**

| | | | |
|---|---|---|---|
| W−N1 | 2.269(6) | W−C1A | 2.276(18) |
| W−C1B | 2.34(3) | W−C2 | 1.930(7) |
| W−C3A | 1.938(14) | W−C3B | 2.01(2) |
| N1−W−C1A | 83.3(5) | N1−W−C1B | 78.6(7) |
| N1−W−C2 | 129.3(3) | N1−W−C3A | 84.6(4) |
| N1−W−C3B | 83.4(7) | C1A−W−C2 | 77.2(5) |
| C1B−W−C2 | 79.1(7) | C1A−W−C3A | 127.6(6) |
| C1B−W−C3B | 122.5(9) | C2−W−C3A | 72.0(5) |
| C2−W−C3B | 71.4(7) | | |

**Synthesis of Silylene Complexes $Cp^*(CO)_2W(Ar)(=SiR_2\cdot DMAP)$ (1a−d) (Ar = Ph, *p*-Tol; R = Me, *p*-Tol).** Aryl(silylene) complexes **1a−d** have been synthesized by two methods: photochemical and nonphotochemical routes (Scheme 2, Table 2). Thus, irradiation ($\lambda > 300$ nm) of a solution of $Cp^*(CO)_3WMe$, arylsilane $HSiR_2Ar$ [$R_2Ar$ = $Me_2Ph$, $Me_2$(*p*-Tol), Me(*p*-Tol)$_2$, and (*p*-Tol)$_3$], and DMAP in toluene or $C_6D_6$ at ca. 5 °C gave silylene complexes $Cp^*(CO)_2W(Ar)(=SiR_2\cdot DMAP)$ [**1a**, Ar = Ph, $R_2$ = $Me_2$; **1b**, Ar = *p*-Tol, $R_2$ = $Me_2$; **1c**, Ar = *p*-Tol, $R_2$ = Me(*p*-Tol); **1d**, Ar = R = *p*-Tol]. The thermal reaction of $Cp^*(CO)_2W(DMAP)Me$ (**2**) with $HSiR_2Ar$ also gave **1a−d** at room temperature. The thermal reaction

(11) (a) Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 7884. (b) Grumbine, S. K.; Straus, D. A.; Tilley, T. D.; Rheingold, A. L. *Polyhedron* **1995**, *14*, 127. (c) Mitchell, G. P.; Tilley, T. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2524. (d) Glaser, P. B.; Tilley, T. D. *Organometallics* **2004**, *23*, 5799. (e) Watanabe, T.; Hashimoto, H.; Tobita, H. *J. Am. Chem. Soc.* **2006**, *128*, 2176.

(12) Suzuki, E.; Okazaki, M.; Tobita, H. *Chem. Lett.* **2005**, 1026.

(13) (a) Sakaba, H.; Ishida, K.; Horino, H. *Chem. Lett.* **1995**, 1145. (b) Sakaba, H.; Ishida, K.; Horino, H. *Chem. Lett.* **1998**, 149. (c) Sakaba, H.; Watanabe, S.; Kabuto, C.; Kabuto, K. *J. Am. Chem. Soc.* **2003**, *125*, 2842. (d) Suzuki, E.; Komuro, T.; Okazaki, M.; Tobita, H. *Organometallics* **2007**, *26*, 4379.

**Scheme 2. Synthesis of Aryl(silylene) Complexes 1a−d**

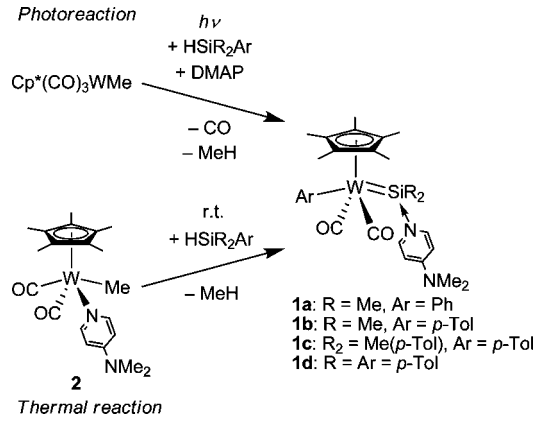



**Table 2. Summary of Isolated Yields of Silylene Complexes 1a−d**

| | photoreaction | | thermal reaction (room temperature) | |
|---|---|---|---|---|
| compound | irradiation time, min | isolated yield, % | time, h | isolated yield, % |
| **1a** | 120 | 42 | 1 | 68 |
| **1b** | 180 | 61 | 1 | 69 |
| **1c** | 150 | 60 | 1 | 71 |
| **1d** | 70 | 34 (NMR yield)[a] | 2 | 66 |

[a] **1d** could not be isolated in the photoreaction because of the difficulty of the separation from unidentified byproduct.

resulted in higher yield in all cases (Table 2). Isolation of complex **1d** from the reaction mixture of the photoreaction was not successful because of the difficulty of the separation of unidentified byproducts from **1d** but was successful in the thermal reaction. These results indicate that the thermal reaction is superior to the photochemical one for the synthesis of **1a−d**.

The aryl(silylene) complexes **1a−d** were characterized on the basis of spectroscopy and elemental analysis. In the $^{29}$Si NMR spectra of **1a−d**, the signals assignable to the silylene silicon atoms were observed at 86.7 (**1a**), 86.5 (**1b**), 83.7 (**1c**), and 85.8 (**1d**) ppm,which are in the typical range for base-stabilized silylenetungsten complexes (62−145 ppm).[3b] The IR spectra of **1a−d** show two bands for a symmetric and an asymmetric CO vibration, where the intensity of the latter band is stronger than that of the former one. This observation implies that the two carbonyl ligands in **1a−d** are mutually in *trans* arrangement.

The crystal structures of complexes **1a** and **1c** have been determined by X-ray crystallography (Figure 2, Table 3). The structure of **1a** has already been reported in the preliminary communications.[12] Complex **1c** adopts a four-legged piano-stool geometry: the tungsten center possesses a pentamethylcyclopentadienyl, a *p*-tolyl, a silylene, and two carbonyl ligands, in which the *p*-tolyl and the silylene ligands are located at mutually *trans* positions. The W−Si bond length [2.505(4) Å] is within the range of those of the base-stabilized silylenetungsten complexes (2.45−2.51 Å).[6] The Si−N1 bond [1.898(11) Å] is comparable to those of nitrogen-donor-coordinated silylene complexes [1.908(2)−2.007(9) Å][3d] and significantly longer than those of normal Si−N covalent bonds (1.70−1.76 Å).[14] The sum of the bond angles between the three bonds except the Si−N1 bond around the silicon atom is 344(2)°, which is in the middle of the tetrahedral (327°) and trigonal (360°) valence

(14) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 3, p 227.

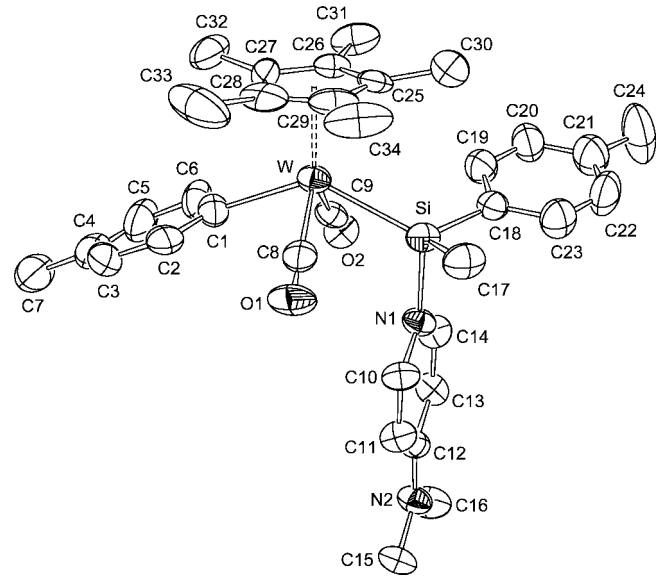
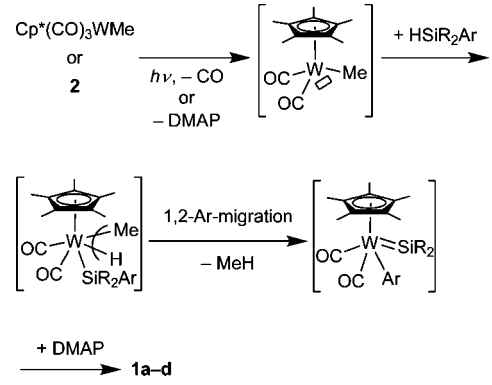



**Figure 2.** ORTEP drawing of **1c**. Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity.

**Table 3. Selected Bond Distances (Å) and Angles (deg) in Cp*(CO)$_2$W(*p*-Tol){=SiMe(*p*-Tol)·DMAP} (1c)**

| | | | |
|---|---|---|---|
| W−Si | 2.505(4) | W−C1 | 2.290(13) |
| W−C8 | 1.945(18) | W−C9 | 1.968(14) |
| Si−N1 | 1.898(11) | | |
| Si−W−C1 | 132.8(4) | Si−W−C8 | 74.2(4) |
| Si−W−C9 | 72.8(4) | C1−W−C8 | 80.8(6) |
| C1−W−C9 | 76.7(5) | C8−W−C9 | 106.0(5) |
| W−Si−N1 | 113.4(4) | W−Si−C17 | 118.8(6) |
| W−Si−C18 | 120.4(4) | C17−Si−C18 | 104.3(7) |

**Scheme 3. A Possible Mechanism for the Formation of Silylene Complexes 1a−d**

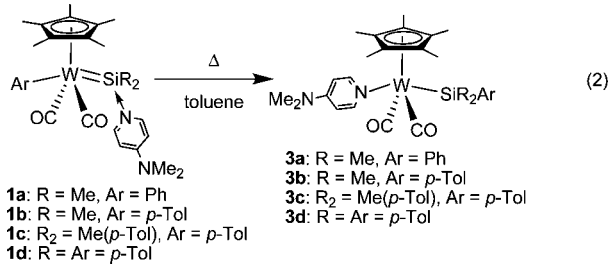



angles. The W−C1 bond length [2.290(13) Å] is within the normal range of W−C(aryl) bond lengths (2.16−2.33 Å).[6]

A possible formation mechanism of **1a−d** is illustrated in Scheme 3. Photochemical dissociation of a CO ligand in Cp*(CO)$_3$WMe or thermal dissociation of the DMAP ligand in **2** generates the 16e methyl complex Cp*(CO)$_2$WMe. Then, oxidative addition of the Si−H bond of arylsilane HSiR$_2$Ar, reductive elimination of methane, 1,2-aryl-migration, and final coordination of a DMAP molecule to the silylene ligand give **1a−d**. In the reactions forming complexes **1a−c**, the alternative process is 1,2-methyl-migration from silicon to tungsten to form methyl(silylene)tungsten complexes, but no signals assignable to the methyl(silylene) complex were observed in the $^1$H NMR spectrum of the reaction mixture. This implies that 1,2-migration of an aryl group is easier than that of a methyl group. A similar

result has been reported on the reaction of iridium complex $Cp^*(PMe_3)Ir(CH_3)(OTf)$ with phenyldimethylsilane that leads exclusively to 1,2-migration of a phenyl group to yield $Cp^*(PMe_3)Ir(Ph)(SiMe_2OTf)$.[4a] Silylene complexes **1a**−**d** were exclusively obtained as the *trans* form where the silylene and the aryl ligands were mutually in *trans* arrangement. We did not observe the corresponding *cis* isomers of **1a**−**d** in the reaction mixture by NMR spectroscopy. This result is possibly attributable to the steric repulsion between the silylene and the aryl ligands, which is larger in the *cis* isomers than in the *trans* forms **1a**−**d**.

**Synthesis of Silyl Complexes 3a−d via Thermal Isomerization of Silylene Complexes 1a−d.** Heating (40−55 °C, 16−72 h) of silylene complexes **1a**−**d** in toluene led to the formation of the corresponding silyl complexes $Cp^*(CO)_2W(DMAP)(SiR_2Ar)$ (**3a**−**d**) in 76−96% yields (eq 2). The 1,2-aryl-migration from tungsten to silicon occurred in these reactions. These results imply that silyl complexes **3a**−**d** are thermodynamically more stable than silylene complexes **1a**−**d**.




(2)

**1a**: R = Me, Ar = Ph
**1b**: R = Me, Ar = *p*-Tol
**1c**: $R_2$ = Me(*p*-Tol), Ar = *p*-Tol
**1d**: R = Ar = *p*-Tol

**3a**: R = Me, Ar = Ph
**3b**: R = Me, Ar = *p*-Tol
**3c**: $R_2$ = Me(*p*-Tol), Ar = *p*-Tol
**3d**: R = Ar = *p*-Tol

Silyl complexes **3a**−**d** were characterized by spectroscopy and elemental analyses. In each of the $^{29}Si$ NMR spectra of **3a**−**d**, one signal appears at 15.8−24.3 ppm that is significantly high-field-shifted compared with those of silylene complexes **1a**−**d** (83.7−86.7 ppm) and is in a typical chemical shift range for silyltungsten complexes (0−70 ppm).[6] The coupling constants between the $^{29}Si$ and $^{183}W$ nuclei of **3a** and **3b** [$^1J_{W-Si}$ = 31 (**3a**), 31 (**3b**) Hz] are considerably smaller than those of the silylene complexes **1a** and **1b** [$^1J_{W-Si}$ = 71 (**1a**), 70 (**1b**) Hz], because the s-character contribution of the orbital of silicon used for formation of the W−Si bond is smaller for silyl complexes **3a,b** than for silylene complexes **1a,b**.

The crystal structures of **3a** and **3d** were determined by X-ray crystallography (Figures 3 and 4, Tables 4 and 5). The structure of **3b** has also been determined and reported in the preliminary communications.[12] Complexes **3a** and **3d** adopt a four-legged piano-stool geometry: the tungsten center possesses one Cp*, one DMAP, one silyl, and two carbonyl ligands, in which one phenyl and two methyl groups (in **3a**) or three *p*-tolyl groups (in **3d**) are bonded to the silicon atom. The silyl and the DMAP ligands are located at mutually *trans* positions, which is consistent with the observation of only one CO resonance in the $^{13}C$ NMR spectra of **3a** and **3d** and also the stronger intensity of the $\nu_{CO}$ band for the asymmetric stretching [1790 (**3a**), 1786 (**3d**) $cm^{-1}$] compared to that for the symmetric band [1876 (**3a**), 1874 (**3d**) $cm^{-1}$] in the IR spectra. The W−Si bond distances in **3a** and **3d** [2.615(2) (**3a**), 2.6110(13) (**3d**) Å] are ca. 0.1 Å longer than those of silylene complexes **1a** and **1c** [2.511(5), 2.534(5) (**1a**);[14] 2.505(4) (**1c**) Å] and are within the range (2.53−2.63 Å) of typical tungsten−silicon single bonds.[6] The Si−W−C(carbonyl) bond angles in **3a** are almost identical [av 69.8(3)°], whereas those in **3d** are substantially different from each other where the Si−W−C1 angle [75.00(16)°] is wider than the Si−W−C2 angle [68.28(14)°]. This geometric difference reflects the large steric hindrance between the Si(*p*-Tol)$_3$ moiety and one CO ligand, i.e., C1 and O1, in **3d**.

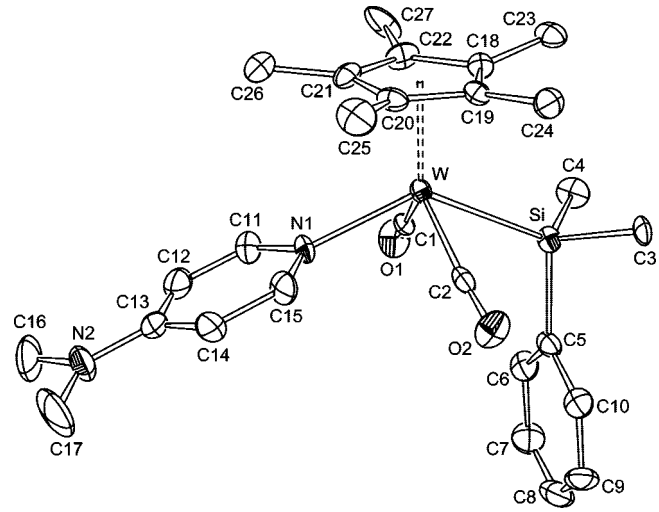



**Figure 3.** ORTEP drawing of **3a**. Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity.

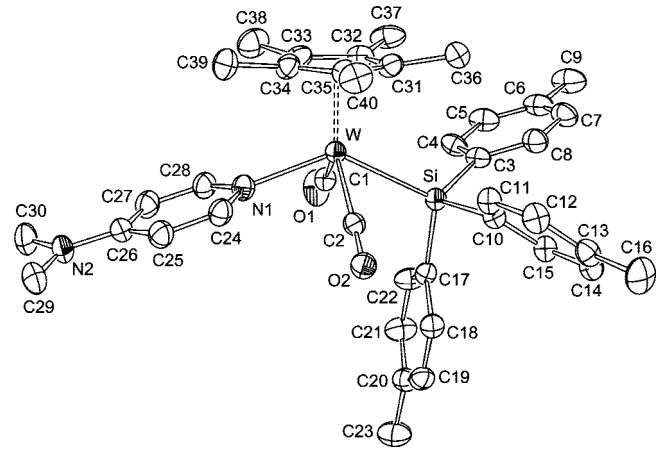



**Figure 4.** ORTEP drawing of **3d**. Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity.

**Table 4. Selected Bond Distances (Å) and Angles (deg) in $Cp^*(CO)_2W(DMAP)(SiMe_2Ph)$ (3a)**

| | | | |
|---|---|---|---|
| W−Si | 2.615(2) | W−N1 | 2.231(8) |
| W−C1 | 1.956(9) | W−C2 | 1.957(9) |
| Si−W−N1 | 132.7(2) | Si−W−C1 | 69.7(3) |
| Si−W−C2 | 69.9(3) | N1−W−C1 | 83.7(3) |
| N1−W−C2 | 84.1(3) | C1−W−C2 | 109.3(4) |
| W−Si−C3 | 115.6(3) | W−Si−C4 | 115.9(3) |
| W−Si−C5 | 114.5(3) | C3−Si−C4 | 104.0(5) |
| C3−Si−C5 | 101.9(4) | C4−Si−C5 | 103.1(4) |

**Table 5. Selected Bond Distances (Å) and Angles (deg) in $Cp^*(CO)_2W(DMAP)\{Si(p\text{-}Tol)_3\}$ (3d)**

| | | | |
|---|---|---|---|
| W−Si | 2.6110(13) | W−N1 | 2.226(4) |
| W−C1 | 1.951(6) | W−C2 | 1.970(5) |
| Si−W−N1 | 133.99(12) | Si−W−C1 | 75.00(16) |
| Si−W−C2 | 68.28(14) | N1−W−C1 | 83.0(2) |
| N1−W−C2 | 80.74(19) | C1−W−C2 | 107.0(2) |
| W−Si−C3 | 116.52(17) | W−Si−C10 | 116.83(16) |
| W−Si−C17 | 112.64(15) | C3−Si−C10 | 103.6(2) |
| C3−Si−C17 | 103.9(2) | C10−Si−C17 | 101.5(2) |

The NMR spectra of the solution of **3c** and **3d** suggest the presence of the hindered rotation around the W–Si bond. The $^1H$ NMR spectrum of **3d** in $C_6D_6$ at room temperature exhibits

**Table 6. Temperature Dependence of Rate Constants ($10^{-5}$ $s^{-1}$) for the Isomerization of Aryl(silylene) Complexes 1a−d to Arylsilyl Complexes 3a−d in $C_6D_6$ at Several Temperatures**

| | temperature | | | | | | |
|---|---|---|---|---|---|---|---|
| compound | 298 K | 303 K | 308 K | 313 K | 318 K | 323 K | 328 K |
| **1a** | | 0.118(2) | | 0.98(4) | 1.96(6) | 4.82(6) | 14.6(5) |
| **1b** | | 0.287(7) | 1.30(2) | 4.74(4) | 17.4(6) | 38.0(8) | |
| **1c** | | | 0.266(5) | 0.53(1) | 2.06(4) | 5.50(8) | 10.7(1) |
| **1d** | 0.36(1) | 0.885(4) | 1.77(4) | 5.4(3) | 10.4(3) | | |

two sets of the signals assignable to the *p*-tolyl groups with 2:1 intensity ratio, indicating that the rotation around the W−Si(*p*-Tol)$_3$ bond is slow on the NMR time scale. This rotation became faster at higher temperature: on raising the temperature to 75 °C, the two sets of the $^1$H NMR signals of the *p*-tolyl groups were merged into one set. On the other hand, the $^1$H NMR spectrum of **3c** in $C_6D_6$ at room temperature shows one set of the signals of the *p*-tolyl groups, indicating that the rotation around the W–SiMe(*p*-Tol)$_2$ bond is fast on the NMR time scale. The variable-temperature $^1$H NMR spectra of **3c** in $CD_2Cl_2$ exhibit temperature-dependent dynamic behavior. One set of the signals of the *p*-tolyl groups (one singlet at 2.24 ppm for the methyl protons and two broad signals at 6.96 and 7.47 ppm for the aromatic protons) are observed in the $^1$H NMR spectrum for the $CD_2Cl_2$ solution of **3c** at 298 K. On cooling the solution to 243 K, the two sets of signals for two rotamers were observed with ca. 6:1 intensity ratio. A similar hindered rotation around the tungsten−silicon bond was reported for the sterically congested tungsten bis(silyl) complex $Cp_2W(SiMe_3)\{Si(t\text{-}Bu)_2H\}$.[15] Thus, the hindered rotation in **3c** and **3d** is also attributable to the steric effect of other ligands on the silyl ligand. The steric hindrance is explicit in the crystal structure of **3d** (Figure 4). The distances between the aryl carbon (C3, C4) on a *p*-Tol group and the methyl carbon (C37) on Cp* [C3···C37, 3.532(8); C4···C37, 3.303(9) Å] and between the aryl carbon (C10, C11) on another *p*-Tol group and the methyl carbon (C36) on Cp* [C10···C36, 3.660(8); C11···C36, 3.451(8) Å] are shorter than the sum (3.7 Å) of the van der Waals radii of a methyl group (2.0 Å) and the half-thickness of the plane of an aromatic ring (1.7 Å).[16] The distance [3.122(8) Å] between the aryl carbon (C22) on a *p*-Tol group and the oxygen (O1) of a CO ligand is comparable to the sum (3.1 Å) of the van der Waals radii of an oxygen atom (1.4 Å) and the half-thickness of the plane of an aromatic ring (1.7 Å).[16] These observations imply the existence of considerable steric repulsion between the Si(*p*-Tol)$_3$ group and the Cp*(CO)$_2$W(DMAP) moiety in **3d**, leading to the hindered rotation around the W−Si(*p*-Tol)$_3$ bond in the solution.

**A Possible Mechanism for the Isomerization of Silylene Complexes 1a−d to Silyl Complexes 3a−d.** To clarify the mechanism of the isomerization of **1a−d** to **3a−d**, a kinetic study was carried out. The rate constants of the isomerization reactions, which obey first-order kinetics, were determined by monitoring the decrease of the intensity of the Cp* signal (for **1a,b,d**) or a signal of the aromatic protons of DMAP (for **1c**) in the $^1$H NMR spectra in $C_6D_6$ at several temperatures from 298 to 328 K (Table 6). The Eyring plots based on the rate constants are shown in Figure 5, and the determined activation parameters are summarized in Table 7.

The large positive values of the activation entropy $\Delta S^{\ddagger}$ [152(9) (**1a**), 307(17) (**1b**), 169(17) (**1c**), and 93(10) (**1d**) J mol$^{-1}$ K$^{-1}$] imply that the isomerization reactions proceed through a dissociative mechanism (Scheme 4). Thus, the thermal isomerization of **1a−d** to **3a−d** is considered to start with dissociation of DMAP from the silylene silicon atom in **1a−d** as the rate-determining step. The resulting base-free silylene complexes **C** undergo 1,2-migration of the aryl group to generate 16-electron silyl complexes **D**, and finally coordination of DMAP to the tungsten center in **D** affords silyl complexes **3a−d**. The unusually large $\Delta S^{\ddagger}$ values suggest the generation of a considerably loose transition state compared to **1a−d**, which is attributable to a nearly complete dissociation of DMAP in the rate-determining step. The activation enthalpy $\Delta H^{\ddagger}$ for the isomerization of **1d** is the smallest among those of **1a−d** [155(3) (**1a**), 199(5) (**1b**), 161(5) (**1c**), and 132(3) (**1d**) kJ mol$^{-1}$]. This result is attributable to the largest steric hindrance of the silylene ligand of **1d** having two *p*-tolyl substituents, which would make the coordination of DMAP the weakest among the silylene complexes **1a−d**.

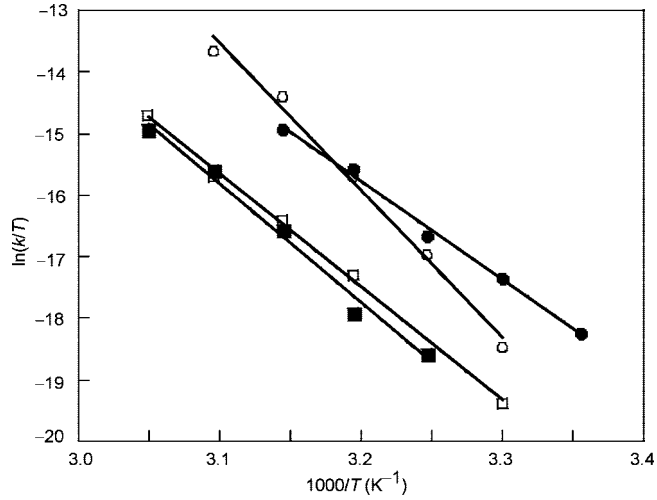
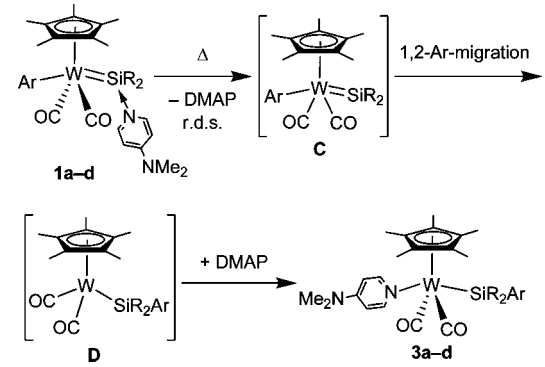



**Figure 5.** Eyring plots [ln (*k*/*T*) vs 1000/*T*] for the isomerization of silylene complexes **1a−d** to silyl complexes **3a−d**: (□) isomerization of **1a**, (○) isomerization of **1b**, (■) isomerization of **1c**, and (●) isomerization of **1d**.

**Table 7. Activation Parameters for the Conversion Reactions of Aryl(silylene) Complexes 1a−d into Arylsilyl Complexes 3a−d in $C_6D_6$**

| compound | $\Delta H^{\ddagger}$, kJ mol$^{-1}$ | $\Delta S^{\ddagger}$, J mol$^{-1}$ K$^{-1}$ | $\Delta G^{\ddagger}_{298}$, kJ mol$^{-1}$ |
|---|---|---|---|
| **1a** | 155(3) | 152(9) | 110(6) |
| **1b** | 199(5) | 307(17) | 108(10) |
| **1c** | 161(5) | 169(17) | 111(10) |
| **1d** | 132(3) | 93(10) | 104(6) |

**Scheme 4. A Possible Mechanism for the Isomerization from Silylene Complexes 1a−d to Silyl Complexes 3a−d**




(15) Koloski, T. S.; Pestana, D. C.; Carroll, P. J.; Berry, D. H. *Organometallics* **1994**, *13*, 489.

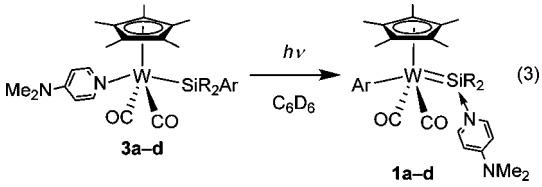
(16) Pauling, L. *The Nature of the Chemical Bonds*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 257−264.

**Table 8. $^1$H NMR Yields of Silylene Complexes 1a−d Derived by the Photoreaction of Silyl Complexes 3a−d in $C_6D_6$**

| compound | irradiation time, min | NMR yield,[a] % | **1a−d**:**3a−d** |
|---|---|---|---|
| **3a** | 1.75 | 63 | 1:0.031 |
| **3b** | 3 | 64 | 1:0.048 |
| **3c**[b] | 0.25 | 41 | 1:0[c] |
| **3d** | 1.25 | 69 | 1:0[c] |

[a] The NMR yields were determined by comparing the intensity of the Cp* signal of **3a−d** in the $^1$H NMR spectra to that of the internal standard [cyclohexane (for **3a**, **3b**, and **3d**) or $Si(SiMe_3)_4$ (for **3c**)]. [b] The concentration of **3c** was about half of the others because of the low solubility of **3c** in $C_6D_6$. [c] No signals of the silyl complex were observed.

**Photoreaction of Silyl Complexes 3a−d.** The 1,2-migration of the aryl group is reversible between the silyl complexes **1a−d** and silylene complexes **3a−d**: irradiation ($\lambda > 300$ nm) of silyl complexes **3a−d** in $C_6D_6$ reproduced the corresponding silylene complexes **1a−d** in 41−69% NMR yields based on $^1$H NMR peak intensities (eq 3, Table 8). These photoisomerization reactions were completed within a few minutes. This result implies that silylene complexes **1a−d** dominate over silyl complexes **3a−d** in the photostationary states. A plausible mechanism for this photochemical isomerization involves photoinduced dissociation of the DMAP ligand in **3a−d**. The dissociation can lead to the 1,2-aryl-migration from the silicon atom to the metal center to generate silylene complexes **C** in Scheme 4, and then the coordination of DMAP to the silylene silicon atom forms **1a−d**. However, an alternative mechanism starting from photoinduced dissociation of a CO ligand in **3a−d** cannot be ruled out.




(3)

## Conclusion

In this work, we investigated the synthesis of DMAP-stabilized aryl(silylene) tungsten complexes **1a−d** and (arylsilyl)(DMAP) tungsten complexes **3a−d**. Complexes **1a−d** were synthesized via 1,2-aryl-migration from 16-electron silyl complexes in the presence of the external base DMAP to stabilize silylene complexes. Silylene complexes **1a−d** isomerized to silyl complexes **3a−d** at 40−55 °C, and UV irradiation of **3a−d** resulted in the reverse isomerization giving **1a−d**. These results indicate that **1a−d** and **3a−d** are interconvertible through 1,2-aryl-migration. The kinetic study on the thermal isomerization of **1a−d** to **3a−d** implies that the dissociation of DMAP is the rate-determining step. Thus, we suggest that possible intermediates in this isomerization reaction are base-free silylene complexes **C** and 16-electron silyl complexes **D** (Scheme 4).

## Experimental Section

**General Procedures.** All manipulations were carried out under dry nitrogen using either a glovebox or both high-vacuum line and standard Schlenk techniques. Benzene-$d_6$, dichloromethane-$d_2$, toluene, hexane, and acetonitrile were dried over calcium hydride and distilled before use. All commercially available reagents were used as received. $Cp^*(CO)_3WMe$ was prepared according to the literature method.[17]

**Physical Measurements.** $^1$H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra were recorded on a Bruker ARX-300 or AVANCE-300 spectrometer. $^{29}Si\{^1H\}$ NMR experiments were performed using the DEPT pulse sequence. The residual proton and the carbon resonances of deuterated solvents were used as internal references for $^1$H and $^{13}$C resonances, respectively. $^{29}Si\{^1H\}$ NMR chemical shifts were referenced to $SiMe_4$ as an external standard. The NMR data were collected at room temperature unless indicated otherwise. Infrared spectra were obtained using a HORIBA FT-730 spectrophotometer. Mass and high-resolution mass spectra were recorded on a Hitachi M-2500S spectrometer operating in the electron impact (EI) mode or a Bruker Daltonics APEX-(III) spectrometer operating in the electrospray ionization (ESI) mode. Mass spectrometric analysis and elemental analysis were performed at the Research and Analytical Center for Giant Molecules, Tohoku University.

**Synthesis of $Cp^*(CO)_2W(DMAP)Me$ (2).** Compound **2** was prepared by modifying a literature method for the synthesis of $Cp^*(CO)_2W(py)Me$ (**A**).[2a] An acetonitrile (5 mL) solution of $Cp^*(CO)_3WMe$ (100 mg, 0.239 mmol) in a Pyrex sample tube with a Teflon vacuum valve was irradiated for 2 h with a 450 W medium-pressure Hg lamp immersed in a water bath (ca. 5 °C). During the photoreaction, the mixture was degassed after 20, 60, and 120 min of irradiation by a conventional freeze−pump−thaw cycle on a vacuum line. The reaction mixture containing $Cp^*(CO)_2W(NCMe)$-Me (**B**) was transferred into a round-bottomed flask and evaporated to dryness under reduced pressure. After addition of DMAP (34 mg, 0.28 mmol) and toluene (5 mL), the mixture was allowed to stand at room temperature for 4.5 h. The reaction mixture was evaporated to dryness, and then the residue was washed with hexane to give a red powder of **2** (105 mg, 0.205 mmol) in 86% yield. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 0.52 (s, 3H, WMe), 1.77 (s, 15H, Cp*), 2.08 (s, 6H, $NMe_2$), 5.53 (m, 2H, py-H), 8.00 (m, 2H, py-H). $^{13}C\{^1H\}$ NMR (75.5 MHz, $C_6D_6$): $\delta$ −2.3 (WMe), 10.7 ($C_5\mathit{Me}_5$), 38.3 ($NMe_2$), 101.9 ($\mathit{C}_5Me_5$), 107.6, 150.5, 155.5 (py), 250.8, 266.2 (CO). IR ($C_6D_6$, $cm^{-1}$): 1898 (s, $\nu_{COsym}$), 1792 (m, $\nu_{COasym}$). Anal. Calcd for $C_{20}H_{28}N_2O_2W$: C, 46.89; H, 5.51; N, 5.47. Found: C, 46.74; H, 5.54; N, 5.37.

**Synthesis of $Cp^*(CO)_2W(Ph)(=SiMe_2\cdot DMAP)$ (1a). Method 1: Photoreaction of a Mixture of $Cp^*(CO)_3WMe$, $HSiMe_2Ph$, and DMAP.** A toluene (8 mL) solution of $Cp^*(CO)_3WMe$ (150 mg, 0.359 mmol), DMAP (50 mg, 0.41 mmol), and $HSiMe_2Ph$ (75 mg, 0.55 mmol) in a Pyrex tube with a Teflon vacuum valve was irradiated for 2 h with a 450 W medium-pressure Hg lamp immersed in a water bath (ca. 5 °C). The reaction mixture was transferred into a round-bottomed flask and cooled at −35 °C. Silylene complex **1a** was obtained as a yellow solid in 42% yield (98 mg, 0.15 mmol).

**Method 2: Reaction of 2 with $HSiMe_2Ph$.** A toluene (4 mL) solution of complex **2** (118 mg, 0.230 mmol) and $HSiMe_2Ph$ (66 mg, 0.48 mmol) was stirred at room temperature for 1 h. The reaction mixture was evaporated to dryness, and the residue was washed with hexane. Recrystallization from toluene/hexane at −35 °C gave **1a** (99 mg, 0.16 mmol) as a yellow powder in 68% yield. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 1.07 (s, 6H, $SiMe_2$), 1.69 (s, 6H, $NMe_2$), 1.92 (s, 15H, Cp*), 5.18 (m, 2H, py-H), 7.17 (m, 1H, *p*-ArH), 7.33 (t, $J$ = 7.3 Hz, 2H, *m*-ArH), 8.08 (m, 2H, *o*-ArH), 8.58 (m, 2H, py-H). $^{13}C\{^1H\}$ NMR (75.5 MHz, $C_6D_6$): $\delta$ 7.6 ($SiMe_2$), 11.5 ($C_5\mathit{Me}_5$), 38.1 ($NMe_2$), 100.7 ($\mathit{C}_5Me_5$), 106.1, 122.5, 127.9, 146.3, 148.4, 149.5, 154.8 (aromatic carbons), 242.7 (CO). $^{29}Si\{^1H\}$ NMR (59.6 MHz, $C_6D_6$): $\delta$ 86.7 ($J_{W-Si}$ = 71 Hz). IR ($C_6D_6$, $cm^{-1}$): 1869 (m, $\nu_{COsym}$), 1784 (s, $\nu_{COasym}$). MS (EI): *m*/*z* 632 ($M^+$, 4), 604 ($M^+$ − CO, 4), 510 ($M^+$ − DMAP, 17). Anal. Calcd for $C_{27}H_{36}N_2O_2SiW$: C, 51.27; H, 5.75; N, 4.43. Found: C, 51.45; H, 5.86; N, 4.32.

(17) Mahmoud, K. A.; Rest, A. J.; Alt, H. G.; Eichner, M. E.; Jansen, B. M. *J. Chem. Soc., Dalton Trans.* **1984**, 175.

**Synthesis of Cp*(CO)$_2$W(*p*-Tol)(=SiMe$_2$·DMAP) (1b). Method 1: Photoreaction of a Mixture of Cp*(CO)$_3$WMe, HSiMe$_2$(*p*-Tol), and DMAP.** A toluene (9.5 mL) solution of Cp*(CO)$_3$WMe (201 mg, 0.481 mmol), DMAP (68 mg, 0.56 mmol), and HSiMe$_2$(*p*-Tol) (107 mg, 0.712 mmol) was irradiated for 3 h in a manner similar to that for **1a**. The reaction mixture was transferred into a round-bottomed flask and concentrated to ca. 6 mL under reduced pressure. Cooling at −35 °C afforded a yellow solid of **1b** in 61% yield (190 mg, 0.294 mmol).

**Method 2: Reaction of 2 with HSiMe$_2$(*p*-Tol).** A toluene (4 mL) solution of **2** (114 mg, 0.222 mmol) and HSiMe$_2$(*p*-Tol) (62 mg, 0.41 mmol) was stirred at room temperature for 1 h. The reaction mixture was evaporated to dryness, and the residue was washed with hexane. Recrystallization from toluene/hexane at −35 °C gave a yellow powder of **1b**·0.5toluene (107 mg, 0.165 mmol) in 69% yield. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 1.08 (s, 6H, SiMe$_2$), 1.70 (s, 6H, NMe$_2$), 1.95 (s, 15H, Cp*), 2.34 (s, 3H, C$_6$H$_4$*Me*), 5.19 (m, 2H, py-H), 7.20 (d, $J$ = 7.4 Hz, 2H, ArH), 8.09 (m, 2H, py-H), 8.49 (d, $J$ = 7.4 Hz, 2H, ArH). $^{13}$C{$^1$H} NMR (75.5 MHz, $C_6D_6$): $\delta$ 7.7 (SiMe$_2$), 11.6 (C$_5$*Me*$_5$), 21.3 (C$_6$H$_4$-*Me*), 38.1 (NMe$_2$), 100.7 (*C*$_5$Me$_5$), 106.1, 128.6, 130.8, 144.0, 146.3, 148.2, 154.8 (aromatic carbons), 242.7 (CO). $^{29}$Si{$^1$H} NMR (59.6 MHz, $C_6D_6$): $\delta$ 86.5 ($J_{W-Si}$ = 70 Hz). IR ($C_6D_6$, cm$^{-1}$) 1869 (w, $\nu_{COsym}$), 1784 (s, $\nu_{COasym}$). MS (ESI): *m*/*z* 669 (M + Na$^+$, 40), 547 (M + Na$^+$ − DMAP, 89). Anal. Calcd for $C_{31.5}H_{42}N_2O_2SiW$ (**1b**·0.5toluene): C, 54.62; H, 6.11; N, 4.04. Found: C, 54.01; H, 5.98; N, 4.11.

**Synthesis of Cp*(CO)$_2$W(*p*-Tol){=SiMe(*p*-Tol)·DMAP} (1c). Method 1: Photoreaction of a Mixture of Cp*(CO)$_3$WMe, HSiMe(*p*-Tol)$_2$, and DMAP.** A toluene (8 mL) solution of Cp*(CO)$_3$WMe (214 mg, 0.512 mmol), DMAP (70 mg, 0.57 mmol), and HSiMe(*p*-Tol)$_2$ (205 mg, 0.906 mmol) was irradiated for 2.5 h in a manner similar to that for **1a**. The reaction mixture was transferred into a round-bottomed flask and concentrated to ca. 3 mL. Hexane (6 mL) was added to the solution, and then the mixture was allowed to stand at room temperature. A yellow solid of a solvate **1c**·0.5toluene was obtained in 60% yield (237 mg, 0.308 mmol).

**Method 2: Reaction of 2 with HSiMe(*p*-Tol)$_2$.** A toluene solution (4 mL) of complex **2** (135 mg, 0.264 mmol) and HSiMe(*p*-Tol)$_2$ (106 mg, 0.468 mmol) was stirred at room temperature for 1 h. The reaction mixture was evaporated to dryness, and then the residue was washed with hexane. Recrystallization from toluene/hexane at −35 °C gave **1c** (136 mg, 0.188 mmol) as a yellow powder in 71% yield. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 1.34 (s, 3H, SiMe), 1.67 (s, 6H, NMe$_2$), 1.81 (s, 15H, Cp*), 2.22 (s, 3H, C$_6$H$_4$*Me*), 2.35 (s, 3H, C$_6$H$_4$*Me*), 5.01 (d, $J$ = 7.8 Hz, 2H, py-H), 7.18−7.26 (m, 4H, ArH), 8.04 (d, $J$ = 7.8 Hz, 2H, ArH), 8.11 (d, $J$ = 7.8 Hz, 2H, ArH), 8.56 (d, $J$ = 7.8 Hz, 2H, py-H). $^{13}$C{$^1$H} NMR (75.5 MHz, $C_6D_6$): $\delta$ 5.9 (SiMe$_2$), 11.3 (C$_5$*Me*$_5$), 21.3, 21.4 (C$_6$H$_4$*Me*), 38.1 (NMe$_2$), 100.6 (*C*$_5$Me$_5$), 106.0, 128.80, 128.82, 131.2, 135.5, 138.3, 143.2, 143.9, 147.6, 147.9, 154.9 (aromatic carbons), 242.0, 243.1 (CO). $^{29}$Si{$^1$H} NMR (59.6 MHz, $C_6D_6$): $\delta$ 83.7. IR (KBr pellet, cm$^{-1}$) 1857 (m, $\nu_{COsym}$), 1759 (s, $\nu_{COasym}$). MS (ESI): *m*/*z* 845 (M + DMAP + H$^+$, 70), 745 (M + Na$^+$, 33), 631 (M$^+$ − *p*-Tol, 100). Anal. Calcd for $C_{37.5}H_{46}N_2O_2SiW$ (**1c**·0.5toluene): C, 58.59; H, 6.03; N, 3.64. Found: C, 58.79; H, 6.04; N, 3.77.

**Synthesis of Cp*(CO)$_2$W(*p*-Tol){=Si(*p*-Tol)$_2$·DMAP} (1d). Method 1: Photoreaction of a Mixture of Cp*(CO)$_3$WMe, HSi(*p*-Tol)$_3$, and DMAP.** A Pyrex NMR tube with a Teflon vacuum valve charged with a $C_6D_6$ (0.5 mL) solution of Cp*(CO)$_3$WMe (10 mg, 0.024 mmol), DMAP (5 mg, 0.04 mmol), HSi(*p*-Tol)$_3$ (10 mg, 0.033 mmol), and cyclohexane (less than 1 mg, internal standard) was attached to a vacuum line. The NMR tube was flame-sealed under high vacuum. The photoreaction was monitored by $^1$H NMR spectroscopy. After irradiation for 70 min with a 450 W medium-pressure Hg lamp immersed in a water bath (ca. 5 °C), silylene complex **1d** was formed in 34% NMR yield. Complex **1d** was not isolated, and the NMR yield was determined by comparing the intensity of the Cp* signal of **1d** in the $^1$H NMR spectrum to that of cyclohexane as an internal standard.

**Method 2: Reaction of 2 with HSi(*p*-Tol)$_3$.** A toluene (4 mL) solution of complex **2** (100 mg, 0.195 mmol) and HSi(*p*-Tol)$_3$ (234 mg, 0.774 mmol) was stirred at room temperature for 2 h. The reaction mixture was concentrated to 3 mL under reduced pressure. Hexane (6 mL) was added to the solution, and the mixture was cooled to −35 °C. A yellow powder of **1d**·0.5toluene was obtained in 66% yield (109 mg, 0.129 mmol). $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 1.61 (s, 6H, NMe$_2$), 1.82 (s, 15H, Cp*), 2.21 (s, 6H, C$_6$H$_4$*Me*), 2.35 (s, 3H, C$_6$H$_4$*Me*), 5.03 (d, $J$ = 7.8 Hz, 2H, py-H), 7.20−7.27 (m, 6H, ArH), 8.00 (d, $J$ = 7.8 Hz, 4H, ArH), 8.32 (d, $J$ = 7.8 Hz, 2H, ArH), 8.59 (d, $J$ = 7.8 Hz, 2H, py-H). $^{13}$C{$^1$H} NMR (75.5 MHz, $C_6D_6$): $\delta$ 11.4 (C$_5$*Me*$_5$), 21.3, 21.4 (C$_6$H$_4$*Me*), 38.0 (NMe$_2$), 100.8 (*C*$_5$Me$_5$), 105.9, 127.9, 128.5, 128.8, 131.2, 137.4, 138.3, 140.4, 147.7, 147.9, 154.9 (aromatic carbons), 241.9 (CO). $^{29}$Si{$^1$H} NMR (59.6 MHz, $C_6D_6$): $\delta$ 85.8. IR (KBr pellet, cm$^{-1}$): 1861 (m, $\nu_{COsym}$), 1763 (s, $\nu_{COasym}$). Anal. Calcd for $C_{43.5}H_{50}N_2O_2SiW$ (**1d**·0.5toluene): C, 61.84; H, 5.97; N, 3.32. Found: C, 62.02; H, 6.08; N, 3.24.

**Synthesis of Cp*(CO)$_2$W(DMAP)(SiMe$_2$Ph) (3a).** A toluene (4 mL) solution of **1a** (82 mg, 0.13 mmol) in a Pyrex tube (12 mm o.d.) with a Teflon vacuum valve was attached to a vacuum line. The tube was flame-sealed under high vacuum and heated at 55 °C for 16 h. The reaction mixture was transferred into a round-bottomed flask and evaporated to dryness. The residue was washed with hexane to give **3a** (73 mg, 0.12 mmol) as a yellow powder in 89% yield. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 1.32 (s, 6H, SiMe$_2$), 1.66 (s, 15H, Cp*), 1.95 (s, 6H, NMe$_2$), 5.33 (m, 2H, py-H), 7.23 (m, 1H, *p*-ArH), 7.39 (t, $J$ = 7.4 Hz, 2H, *m*-ArH), 8.24 (m, 2H, *o*-ArH), 8.34 (m, 2H, py-H). $^{13}$C{$^1$H} NMR (75.5 MHz, $C_6D_6$): $\delta$ 6.1 (SiMe$_2$), 10.9 (C$_5$*Me*$_5$), 38.0 (NMe$_2$), 101.1 (*C*$_5$Me$_5$), 108.1, 127.3, 127.9, 135.7, 150.2, 153.2, 159.4 (aromatic carbons), 243.1 (CO). $^{29}$Si{$^1$H} NMR (59.6 MHz, $C_6D_6$): $\delta$ 15.8 ($J_{W-Si}$ = 31 Hz). IR ($C_6D_6$, cm$^{-1}$) 1876 (m, $\nu_{COsym}$), 1790 (s, $\nu_{COasym}$). MS (ESI): *m*/*z* 1287 (M$_2$ + Na$^+$, 12), 655 (M + Na$^+$, 42), 533 (M + Na$^+$ − DMAP, 74). Anal. Calcd for $C_{27}H_{36}N_2O_2SiW$: C, 51.27; H, 5.75; N, 4.43. Found: C, 51.64; H, 5.74; N, 4.26.

**Synthesis of Cp*(CO)$_2$W(DMAP){SiMe$_2$(*p*-Tol)} (3b).** A sealed tube (12 mm o.d.) of a toluene (4 mL) solution of **1b** (80 mg, 0.12 mmol), prepared in a manner similar to that for the synthesis of **3a**, was heated at 40 °C for 72 h. The reaction mixture was transferred into a round-bottomed flask and evaporated to dryness. The residue was washed with hexane to give **3b** (61 mg, 0.095 mmol) as a yellow powder in 76% yield. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 1.33 (s, 6H, SiMe$_2$), 1.68 (s, 15H, Cp*), 1.97 (s, 6H, NMe$_2$), 2.26 (s, 3H, C$_6$H$_4$*Me*), 5.35 (m, 2H, py-H), 7.23 (d, $J$ = 7.2 Hz, 2H, ArH), 8.21−8.28 (m, 4H, ArH and py-H). $^{13}$C{$^1$H} NMR (75.5 MHz, $C_6D_6$): $\delta$ 6.3 (SiMe$_2$), 10.9 (C$_5$*Me*$_5$), 21.4 (C$_6$H$_4$*Me*), 38.0 (NMe$_2$), 101.1 (*C*$_5$Me$_5$), 108.1, 128.1, 135.8, 136.2, 146.4, 153.2, 159.4 (aromatic carbons), 243.1 (CO). $^{29}$Si{$^1$H} NMR (59.6 MHz, $C_6D_6$): $\delta$ 15.8 ($J_{W-Si}$ = 31 Hz). IR ($C_6D_6$, cm$^{-1}$): 1876 (w, $\nu_{COsym}$), 1790 (s, $\nu_{COasym}$). MS (ESI): *m*/*z* 1315 (M$_2$ + Na$^+$, 23), 669 (M + Na$^+$, 51), 547 (M$^+$ + Na$^+$ − DMAP, 100). Anal. Calcd for $C_{28}H_{38}N_2O_2SiW$: C, 52.01; H, 5.92; N, 4.35. Found: C, 51.77; H, 5.84; N, 4.30.

**Synthesis of Cp*(CO)$_2$W(DMAP){SiMe(*p*-Tol)$_2$} (3c).** A sealed tube (12 mm o.d.) of a toluene (4 mL) solution of **1c**·0.5toluene (65 mg, 0.085 mmol), prepared in a manner similar to that for the synthesis of **3a**, was heated at 50 °C for 64 h. The reaction mixture was transferred into a round-bottomed flask and evaporated to dryness. The residue was washed with hexane to afford **3c** (56 mg, 0.077 mmol) as a yellow powder in 91% yield. $^1$H NMR (300 MHz, $C_6D_6$, room temparature): $\delta$ 1.51 (br, 3H, SiMe), 1.66 (s, 15H, Cp*), 1.96 (s, 6H, NMe$_2$), 2.17 (br, 6H, C$_6$H$_4$*Me*), 5.34 (m, 2H, py-H),

**Table 9. Crystallographic Data for 1c, 2, 3a, and 3d**

| | **1c**·0.5$C_7H_8$ | **2**·0.5$C_7H_8$ | **3a** | **3d**·2$C_6D_6$ |
|---|---|---|---|---|
| formula | $C_{37.5}H_{46}N_2O_2SiW$ | $C_{23.5}H_{32}N_2O_2W$ | $C_{27}H_{36}N_2O_2SiW$ | $C_{52}H_{58}N_2O_2SiW$ |
| formula wt | 768.70 | 558.36 | 632.52 | 954.94 |
| cryst size, mm | 0.29 × 0.21 × 0.10 | 0.20 × 0.20 × 0.03 | 0.19 × 0.11 × 0.11 | 0.35 × 0.34 × 0.20 |
| cryst color | yellow | red | yellow | yellow |
| cryst syst | monoclinic | monoclinic | monoclinic | triclinic |
| space group | *C*2/*c* (No. 15) | $P2_1/n$ (No. 14) | *P*2/*a* (No. 13) | *P*-1 (No. 2) |
| *a*, Å | 32.348(7) | 8.7537(3) | 17.6549(13) | 11.2137(2) |
| *b*, Å | 9.7497(16) | 21.3505(6) | 8.6900(6) | 12.3983(2) |
| *c*, Å | 24.761(4) | 12.2441(3) | 17.7595(15) | 18.9190(9) |
| α, deg | | | 89.2410(13) | |
| *β*, deg | 117.067(6) | 97.3584(17) | 104.716(4) | 75.7590(7) |
| *γ*, deg | | | 65.4601(13) | |
| *V*, Å$^3$ | 6954(2) | 2269.53(11) | 2635.3(3) | 2307.38(12) |
| *Z* | 8 | 4 | 4 | 2 |
| $D_{calcd}$, g cm$^{-3}$ | 1.468 | 1.634 | 1.594 | 1.374 |
| *F*(000) | 3112 | 1108 | 1264 | 976 |
| $\mu$(Mo Kα), mm$^{-1}$ | 3.39 | 5.11 | 4.45 | 2.57 |
| reflections collected | 17256 | 21951 | 21289 | 21990 |
| unique reflections ($R_{int}$) | 7167 (0.112) | 5204 (0.064) | 5888 (0.132) | 10481 (0.068) |
| refined parameters | 391 | 251 | 307 | 473 |
| *R*1, *wR*2 (all data) | 0.117, 0.243 | 0.055, 0.118 | 0.093, 0.128 | 0.057, 0.142 |
| *R*1, *wR*2 [$I > 2\sigma(I)$] | 0.079, 0.199 | 0.042, 0.106 | 0.073, 0.121 | 0.051, 0.133 |
| GOF | 1.16 | 1.28 | 1.19 | 1.15 |
| largest residual peak, hole, e Å$^{-3}$ | 1.27, −2.52 | 1.34, −1.78 | 2.52, −2.31 | 3.48, −3.71 |

8.18 (d, $J$ = 7.7 Hz, 4H, ArH), 8.28 (m, 2H, py-H).[18] $^1$H NMR (300 MHz, $CD_2Cl_2$, 298 K): $\delta$ 0.78 (s, 3H, SiMe), 1.60 (s, 15H, Cp*), 2.24 (s, 6H, $C_6H_4$*Me*), 3.00 (s, 6H, $NMe_2$), 6.35 (m, 2H, py-H), 6.96 (br, 4H, ArH), 7.47 (br, 4H, ArH), 8.26 (m, 2H, py-H).[18] $^1$H NMR (300 MHz, $CD_2Cl_2$, 243 K, major rotamer): $\delta$ 0.68 (s, 3H, SiMe), 1.53 (s, 15H, Cp*), 2.11 (s, 3H, $C_6H_4$*Me*), 2.25 (s, 3H, $C_6H_4$*Me*), 2.97 (s, 6H, $NMe_2$), 6.31 (d, $J$ = 7.4 Hz, 2H, py-H), 6.83 (d, $J$ = 7.7 Hz, 2H, ArH), 7.02 (d, $J$ = 7.7 Hz, 2H, ArH), 7.21 (d, $J$ = 7.7 Hz, 2H, ArH), 7.57 (d, $J$ = 7.7 Hz, 2H, ArH), 8.18 (d, $J$ = 7.4 Hz, 2H, py-H).[18] $^{13}$C{$^1$H} NMR (75.5 MHz, $CD_2Cl_2$, 243 K, major rotamer): $\delta$ 2.6 (SiMe), 10.3 ($C_5$*Me*$_5$), 20.8, 20.9 ($C_6H_4$-*Me*), 39.1 ($NMe_2$), 101.3 ($C_5Me_5$), 108.3, 127.1, 127.3, 135.4, 135.7, 136.1, 136.4, 143.4, 144.5, 153.1, 158.6 (aromatic carbons), 221.1, 243.0 (CO).[18] $^{29}$Si{$^1$H} NMR (59.6 MHz, $CD_2Cl_2$, 243 K, major rotamer): $\delta$ 17.8.[18] IR (KBr pellet, cm$^{-1}$) 1880 (m, $\nu_{COsym}$), 1786 (s, $\nu_{COasym}$). Anal. Calcd for $C_{34}H_{42}N_2O_2SiW$: C, 56.51; H, 5.86; N, 3.88. Found: C, 56.50; H, 5.84; N, 3.73.

**Synthesis of Cp*(CO)$_2$W(DMAP){Si(*p*-Tol)$_3$} (3d).** A sealed tube (12 mm o.d.) of a toluene (3 mL) solution of **1d** (79 mg, 0.099 mmol), prepared in a manner similar to that for the synthesis of **3a**, was heated at 40 °C for 44 h. The reaction mixture was transferred into a round-bottomed flask and evaporated to dryness. The residue was washed with hexane to give **3d** (76 mg, 0.095 mmol) as a yellow powder in 96% yield. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 1.68 (s, 15H, Cp*), 1.95 (s, 6H, $NMe_2$), 2.03 (s, 3H, $C_6H_4$-*Me*), 2.24 (s, 6H, $C_6H_4$*Me*), 5.34 (m, 2H, py-H), 7.05 (d, $J$ = 7.7 Hz, 2H, ArH), 7.22 (d, $J$ = 7.7 Hz, 4H, ArH), 8.17 (d, $J$ = 7.7 Hz, 4H, ArH), 8.26 (d, $J$ = 7.7 Hz, 2H, ArH), 8.29 (m, 2H, py-H). $^{13}$C{$^1$H} NMR (75.5 MHz, $C_6D_6$): $\delta$ 10.9 ($C_5$*Me*$_5$), 21.2, 21.5 ($C_6H_4$*Me*), 38.0 ($NMe_2$), 101.5 ($C_5Me_5$), 108.3, 127.9, 128.9, 136.0, 136.7, 137.5, 138.8, 141.6, 144.8, 153.3, 159.1 (aromatic carbons), 244.2 (CO). $^{29}$Si{$^1$H} NMR (59.6 MHz, $C_6D_6$): $\delta$ 24.3. IR (KBr pellet, cm$^{-1}$) 1874 (m, $\nu_{COsym}$), 1786 (s, $\nu_{COasym}$). Anal. Calcd (%) for $C_{40}H_{46}N_2O_2SiW$: C, 60.15; H, 5.80; N, 3.51. Found: C, 60.52; H, 5.82; N, 3.38.

**Kinetic Study on the Thermal Reaction of Silylene Complexes 1a−d to Form Silyl Complexes 3a−d.** A Pyrex NMR tube equipped with a ground joint was charged with a solution of silylene complex **1a** (2 mg, 3 $\mu$mol) and cyclohexane (less than 1 mg, internal standard) in benzene-$d_6$ (0.5 mL). This NMR tube was attached to a vacuum line and flame-sealed under high vacuum. Five sealed NMR sample tubes were prepared in this method. Each sealed tube was heated at 30, 40, 45, 50, or 55 °C, and the reaction was monitored by $^1$H NMR spectroscopy. The ratio of the intensity of the Cp* signal of **1a** against the initial intensity, which is equivalent to the ratio of their concentrations [**1a**]/[**1a**]$_0$, was fitted to first-order plots of ln [**1a**]/[**1a**]$_0$ versus time according to the following equation: ln [**1a**]/[**1a**]$_0$ = $-kt$. The rate constants $k$ at the corresponding temperatures were determined from the slopes.

The rate constants for the thermal reactions of silylene complexes **1b−d** were determined in a manner similar to that for **1a**.[19] For **1c**, the intensity of a signal of the aromatic protons of DMAP in the $^1$H NMR spectrum was used for the determination of the rate constants. The results are summarized in Table 6.

**Monitoring the Photoreaction of Silyl Complexes 3a−d to Give Silylene Complexes 1a−d.** A Pyrex NMR tube equipped with a ground joint was charged with a solution of silyl complex **3a** (2 mg, 3 $\mu$mol) and cyclohexane (less than 1 mg, internal standard) in benzene-$d_6$ (0.5 mL). This NMR tube was attached to a vacuum line and flame-sealed under high vacuum. The sealed tube was irradiated with a 450 W medium-pressure Hg lamp immersed in a water bath (ca. 5 °C), and the reaction was monitored by $^1$H NMR spectroscopy. After irradiation for 1.75 min, the intensity of the signal assignable to silylene complex **1a** reached to a maximum (63% NMR yield, **1a**:**3a** = 32:1).

Photoreactions of silyl complex **3b−d** were monitored by a method analogous to that for **3a**. For **3c**, $Si(SiMe_3)_4$ (less than 1 mg) instead of cyclohexane was used as the internal standard. The concentration of **3c** was about a half of other silyl complexes **3a**, **3b**, and **3d** because of its low solubility in $C_6D_6$. The NMR yields were determined by comparing the intensity of the Cp* signal of **3a−d** in the $^1$H NMR spectra to that of the internal standard. The results are summarized in Table 8.

**X-Ray Crystal Structure Determination.** Selected crystallographic data for **1c**, **2**, **3a**, and **3d** are summarized in Table 9. X-ray quality single crystals were obtained from toluene (for **1c**·0.5$C_7H_8$ and **2**·0.5$C_7H_8$ as yellow plates and red plates, respectively), toluene/hexane (for **3a** as yellow plates), and benzene-$d_6$ (for **3d**·2$C_6D_6$ as yellow plates). Intensity data for the analysis were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite monochromated Mo Kα radiation ($\lambda$ = 0.71069 Å) under a cold nitrogen stream ($T$ = 150 K). Numerical absorption

(18) Signals of four aromatic protons were overlapped with that of $C_6D_5H$ because complex **3c** is only slightly soluble in $C_6D_6$. The low solubility of **3c** in $C_6D_6$ prevents us from measuring the $^{13}$C and $^{29}$Si NMR spectra in $C_6D_6$. Thus, a $CD_2Cl_2$ solution was used to measure the $^{13}$C and $^{29}$Si NMR spectra of the major rotamer at 243 K. **3c** is fluxtional in $C_6D_6$ and $CD_2Cl_2$ solutions (see text).

corrections were applied to the data. The structures were solved by the Patterson method using the DIRDIF-99 program[20] and refined by full matrix least-squares techniques on all $F^2$ data with SHELXL-97.[21] For **2**, the sites of the methyl ligand and a carbonyl ligand were mutually disordered with the occupancy factors 61:39. In the case of **1c** and **2**, a toluene molecule, solvent of crystallization, was disordered over two sites related by a 2-fold rotation axis (for **1c**) or an inversion center (for **2**). Except for the solvent molecules and the disordered atoms, anisotropic refinement was applied to all non-hydrogen atoms, and all hydrogen atoms were put at calculated positions. The disordered atoms and the atoms of the crystal solvents were isotropically refined, and no hydrogen atoms on these atoms were included. In the final difference Fourier synthesis of silyl complex **3d**, the residual peak of 3.48 e $Å^{-3}$ was observed within 0.87 Å of the tungsten atom. CCDC reference numbers: 714828 (**1c**), 714829 (**2**), 714830 (**3a**), and 714831 (**3d**). Crystallographic data are available as a CIF.

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**Supporting Information Available:** X-ray crystallographic data as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) When we monitored the thermal reaction of **1d** by $^1$H NMR spectroscopy, we observed the signals of unidentified reaction intermediates, which finally completely changed to silyl complex **3d**.

(20) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. *The DIRDIF-99 Program System*; Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 1999.

(21) Sheldrick, G. M. *SHELXL-97, Programs for Refining X-ray Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.