# Synthesis of Self-Stabilized and Donor-Free Silyl(silylene)tungsten Complexes

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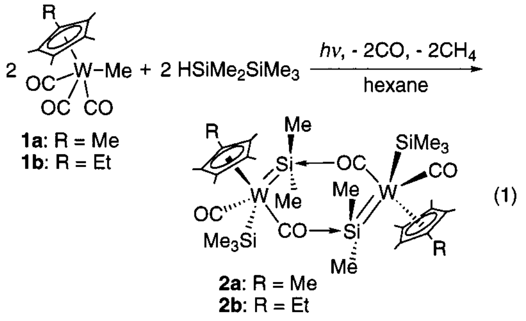
*Summary: Photolysis of* $Cp'W(CO)_3Me$ (***1a***, $Cp' = \eta$-$C_5Me_5$; ***1b***, $Cp' = \eta$-$C_5Me_4Et$) *in the presence of excess* $HSiMe_2SiMe_3$ *afforded a self-stabilized silyl(silylene)tungsten complex with a dimeric structure,* $[Cp'W(CO)_2({=}SiMe_2)(SiMe_3)]_2$ (***2a***, $Cp' = \eta$-$C_5Me_5$; ***2b***, $Cp' = \eta$-$C_5Me_4Et$), *respectively. In contrast, photolysis of* ***1a*** *in the presence of* $HSiMe_2SiMeMes_2$ ($Mes = 2,4,6$-$Me_3C_6H_2$) *resulted in the formation of the first donor-free silyl(silylene) complex with only alkyl and aryl substituents on the silicon atoms,* $Cp'W(CO)_2({=}SiMes_2)(SiMe_3)$ (***3***).

Considerable attention has been focused on the synthesis and chemical behavior of silylene−transition metal complexes.[1,2] Silyl(silylene) complexes $L_nM({=}SiR_2)$-$SiR_3$ are one of the attractive synthetic targets since such complexes have been assumed to be key intermediates in many transition metal-catalyzed scrambling of substituents and skeletal redistribution of organosilicon and organosilicon−transition metal compounds.[2,3] Silyl(silylene) complexes have been isolated as internal or external donor-stabilized complexes in which the electron-deficient silylene ligands are stabilized by coordination of two-electron donors.[4−7] Lappert et al. very recently reported the synthesis of the first donor-free silyl(silylene) complex by the reaction of an isolable silylene and a platinum complex.[8] The silylene ligand in this complex is stabilized electronically by delocalization of lone pair electrons of two amino substituents attached to the silicon atom. There has been no base-free silyl(silylene) complexes with only alkyl or aryl groups on the silicon atoms.

In our previous work on donor-stabilized silyl(silylene)[6,7] and donor-free germyl(germylene)tungsten complexes,[9] we found that the tungsten fragment $Cp'W(CO)_2$ ($Cp' = \eta$-$C_5Me_5$, $\eta$-$C_5H_5$) stabilizes the $R_3E{-}M{=}ER_2$ framework efficiently (E = Si, Ge; M = metal fragment). This prompted us to synthesize *base-free* silyl(silylene)tungsten complexes. Here we report the photolysis of a methyltungsten complex in the presence of hydrodisilanes. This reaction afforded either a monomeric *base-free* silyl(silylene)tungsten complex or a self-stabilized dimer of a silyl(silylene)tungsten complex depending on the sustituents on the silicon atoms.

Photolysis of $Cp'W(CO)_3Me$ (**1a**, $Cp' = Cp^*$, $Cp^* = \eta$-$C_5Me_5$; **1b**, $Cp' = \eta$-$C_5Me_4Et$) in the presence of excess $HSiMe_2SiMe_3$ in hexane afforded yellow crystals of a self-stabilized silyl(silylene)tungsten complex with a dimeric structure, $[Cp'W(CO)_2({=}SiMe_2)(SiMe_3)]_2$ (**2a**, $Cp' = Cp^*$; **2b**, $Cp' = \eta$-$C_5Me_4Et$) in 87 and 54% yield, respectively (eq 1). Crystal structure analysis confirmed that complex **2b** is the first silylene complex stabilized by coordination of an isocarbonyl ligand, which is coordinated to a tungsten fragment and a silylene ligand via its carbon and oxygen atom, respectively (Figure 1). The tungsten−silylene bond (W−Si(2) 2.489(2) Å) is significantly shorter than the tungsten−silyl bond (W−Si(1) 2.609(2) Å), indicating partial double bond character for the W−Si(2) bonding. The silylene ligand is



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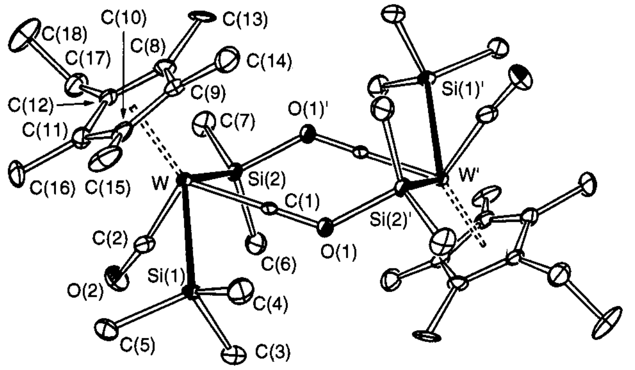


**Figure 1.** ORTEP drawing of complex **2b**. Thermal ellipsoids are drawn at the 50% probability level.

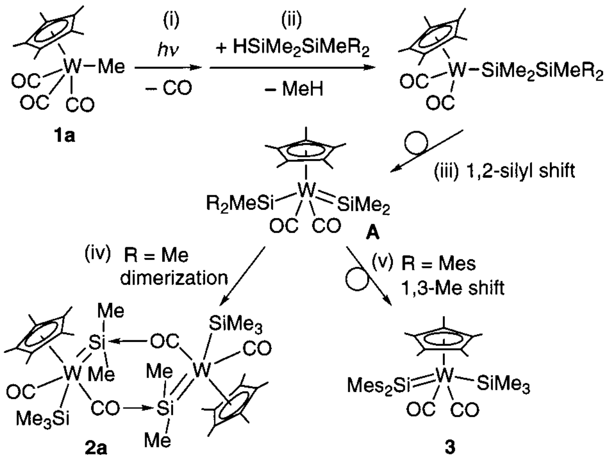
pyramidalized due to the coordination of carbonyl oxygen (sum of the three valence bond angles around Si(2) = 335.1(6)°). The Si(2)−O(1)′ distance (1.823(5) Å) is significantly longer than those of usual Si−O single bonds (1.58−1.70 Å)[10] and even slightly longer than those reported for donor-stabilized silyl(silylene)tungsten complexes (1.774(6)−1.792(7) Å).[6,7]

The dimeric structure of **2** is maintained even in solution. The $^{29}$Si NMR spectrum of **2a** in $C_6D_6$ showed two peaks at 23.5 and 100.0 ppm which are assignable to the silyl and silylene ligands, respectively. The low-field shift of the latter signal is characteristic of donor-stabilized silylene complexes and comparable to those reported for donor-stabilized silylenetungsten complexes ($\delta$ 62−145 ppm).[6,7,11] The IR spectrum of complex **2a** gives two carbonyl stretching bands at 1884 and 1556 cm$^{-1}$. The significant low-frequency shift of the latter absorption clearly demonstrates the existence of the isocarbonyl group.[12] Heating a mixture of **2a** and **2b** in toluene-$d_8$ at 80 °C for 5 h did not afford the mixed dimer [Cp*W(CO)$_2$(=SiMe$_2$)(SiMe$_3$)·($\eta$-C$_5$Me$_4$Et)W(CO)$_2$(=SiMe$_2$)(SiMe$_3$)] at all.

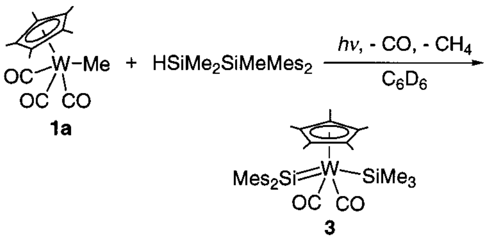
Scheme 1 shows a possible formation mechanism of complex **2a**: (i) photochemical elimination of a carbonyl group from **1a**, (ii) oxidative addition of HSiMe$_2$SiMe$_3$ and reductive elimination of CH$_4$ to give a 16-electron disilanyltungsten intermediate, (iii) 1,2-silyl shift to form a silyl(silylene)tungsten intermediate **A**, and (iv) dimerization of **A** to give the final product **2a**. In our previous paper, we have reported that the corresponding germyl(germylene)tungsten complex Cp*W(OC)$_2$(=GeMe$_2$)GeMe$_3$ exists as a monomeric donor-free form.[9] This strikingly contrasts with the formation of self-stabilized dimeric silyl(silylene)tungsten complex **2** and demonstrates the instability of the silylene complex and strong Lewis acidity of the silylene ligand.

To prevent the dimerization and stabilize the donor-free silyl(silylene)tungsten complex, bulky substituents were introduced on the silicon atoms. After several attempts, we found that photolysis of Cp*W(CO)$_3$Me

### Scheme 1



(**1a**) in the presence of HSiMe$_2$SiMeMes$_2$ (Mes = mesityl group (2,4,6-Me$_3$C$_6$H$_2$)) resulted in the formation of donor-free silyl(silylene)tungsten complex Cp*W(CO)$_2$(=SiMes$_2$)(SiMe$_3$) (**3**), which was isolated as yellow crystals in 40% yield (eq 2). Complex **3** is the first *donor-free* silyl(silylene) complex with only alkyl and aryl substituents on the silicon atoms.



(2)

Complex **3** showed $^{29}$Si NMR signals at 22.1 and 380.9 ppm, which are assignable to silyl and silylene ligands, respectively. The remarkable low-field shift of the silylene signal clearly demonstrates that complex **3** contains a three-coordinate, sp$^2$-hybridized silicon atom. Similar low-field shifts of silylene signals of donor-free silylene complexes have been reported by Tilley et al.[13] The IR spectrum shows two CO stretching absorptions in the terminal CO region (1900 and 1840 cm$^{-1}$), which is consistent with the absence of the isocarbonyl ligand.

The structure of complex **3** was confirmed by crystal structure analysis (Figure 2). The tungsten−silylene bond (W−Si(1) 2.3850(12) Å) is remarkably shorter than the tungsten−silyl bond in the same molecule (W−Si(2) 2.6456(13) Å). This is even shorter than the tungsten−silylene bond in complex **2b** (2.489(2) Å) and, to our knowledge, the shortest W−Si bonding reported so far. The geometry around the silicon atom of the silylene ligand is planar (sum of the three bond angles around Si(1) = 359.9(3)°). These results clearly show the double bond character of the tungsten−silylene bonding. The

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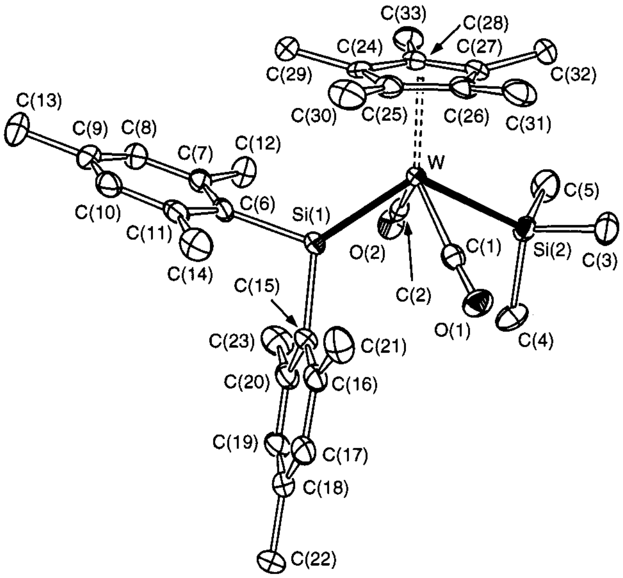

**Figure 2.** ORTEP drawing of complex **3**. Thermal ellipsoids are drawn at the 50% probability level.

double bond character of W–Si(1) bonding is further supported by the large tungsten–silicon coupling constant ($^1J_{\mathrm{SiW}} = 154.9$ Hz) observed for the silylene ligand compared to that for the silyl ligand ($^1J_{\mathrm{SiW}} = 30.5$ Hz) in the same molecule. The former value is even larger than those reported for the donor-stabilized silylene-tungsten complexes ($^1J_{\mathrm{SiW}} = 92-132$ Hz).[6,7,11]

It should be noted that, in complex **3**, two mesityl groups are localized on the silylene ligand. Thus, 1,3-Me migration must take place from silyl to silylene ligand in silyl(silylene) intermediate **A** to give complex **3** as the final product (step v in Scheme 1). Conversion of **A** to **3** apparently reduces steric congestion in **A**. This type of 1,3-substituent migration has been directly observed in donor-stabilized silyl(silylene)iron and -tungsten complexes and established as a feature exhibited by silyl(silylene) complexes.[2,5,7]

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**Supporting Information Available:** Experimental details and spectroscopic data of **2a**, **2b**, and **3** and details of crystal structure determinations and structure data for **2b** and **3** (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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