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Synthesis, Structure, and Fluxional Behavior of Base-Stabilized Silyl(silylene)tungsten Complexes

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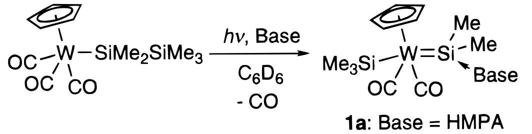
Summary: Donor-stabilized silyl(silylene)tungsten complexes $Cp(OC)_2W(SiMe_3)({=}SiMe_2{\cdot}Base)$ *(Cp =* η*-*C_5H_5*, Base = HMPA (**1a**) and THF (**1b**)) have been synthesized by photolysis of* C_6D_6 *solutions containing* $CpW(CO)_3SiMe_2SiMe_3$ *and bases. The double-bond character of the tungsten−silylene bonding was revealed by the significant downfield shift of the* ^{29}Si *NMR signal as well as the large* $^1J_{WSi}$ *value for the silylene ligand (*δ *= 92.5 ppm (*$^1J_{WSi}$ *= 121 Hz) for **1a** and* δ *= 144.7 ppm (*$^1J_{WSi}$ *= 132 Hz) for **1b**) and also the short W−Si distance between tungsten and the silylene ligand (2.481(3) Å) of **1a**. Complex **1b** shows fluxional behavior due to intramolecular 1,3-methyl migration from the silyl ligand to the silylene ligand.*

It has been known for many years that transition-metal complexes catalyze the redistribution of substituents on silicon atoms in organosilicon compounds.[1,2] Silylene complexes have often been postulated to account for the transition-metal-catalyzed redistribution.[1,3] A possible mechanism for the redistribution involves the formation of an intermediate silyl(silylene)-metal complex of the type $L_nM({=}SiR_2)SiR_3$ followed by the *intramolecular* 1,3-substituent migration from the silyl group to the silylene ligand in the silyl(silylene) complex. Pannell,[4] the present authors,[5] Turner,[6] and others[7] have reported convincing evidence for the formation of silyl(silylene) intermediates and the 1,3-migration process in the silyl(silylene) complexes. However, attempts to isolate the silyl(silylene) intermediate have not been successful due to its thermal instability, although intramolecularly base-stabilized silyl(silylene)-metal complexes[8,9] and photolabile silyl(silylene)iron complexes stabilized by complexation to chromium carbonyl[10] have been reported.

Very recently, we have isolated an external base-stabilized silyl(silylene)iron complex and directly observed 1,3-methyl migration from the silyl group to the silylene ligand using a VT NMR technique.[11] However, the extreme sensitivity of the complex toward air and moisture prevented further investigation, such as crystal structure determination and reactivity studies. Thus, we have sought a stable silyl(silylene)metal system. Here, we report the synthesis of the first external base-stabilized silyl(silylene)tungsten complexes $Cp(OC)_2W(SiMe_3)({=}SiMe_2{\cdot}Base)$ (Cp = η-C_5H_5, Base = HMPA (hexamethylphosphoric triamide, **1a**) and THF (**1b**)). The tungsten complexes are relatively stable compared to the iron complex. The crystal structure of **1a** and the fluxional behavior of complex **1b** are also reported.

Irradiation of a C_6D_6 solution containing $CpW(CO)_3SiMe_2SiMe_3$ (**2**)[12] and 3 equiv of THF in a Pyrex NMR sample tube with a 450 W medium-pressure mercury arc lamp afforded a THF-coordinated silyl(silylene)tungsten complex **1b** almost quantitatively (eq 1).[13] The HMPA-coordinated silyl(silylene)tungsten complex **1a** was synthesized by a similar procedure.[14] However, in this case, a small amount of unidentified byproduct was



(1)

1a: Base = HMPA
1b: Base = THF

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[13] **1b**: A toluene solution (ca. 3 mL) of **2** (0.10 g, 0.22 mmol) and THF (0.5 mL) placed in the Pyrex sample tube described above was irradiated for 1 h. After irradiation, volatiles were removed from the reaction mixture under reduced pressure. The residue was recrystallized from toluene/hexane to afford pale yellow crystals of **1b** (0.022 g, 0.043 mmol, 20%): ^1H NMR (300 MHz, THF-d_8, room temperature) δ 5.03 (s, 5H, Cp), 0.73 (s, 6H, $SiMe_2$), 0.36 (s, 9H, $SiMe_3$); ^{13}C NMR (75.5 MHz, THF-d_8, room temperature) δ 226.5 (CO), 87.7 (Cp), 9.8 ($SiMe_2$), 6.7 ($SiMe_3$); ^{29}Si NMR (59.6 MHz, THF-d_8, room temperature) δ 144.7 ($^1J_{WSi}$ = 132 Hz, $SiMe_2$), 18.2 ($^1J_{WSi}$ = 54 Hz, $SiMe_3$); IR (THF-d_8) ν_{CO} 1868, 1792 cm^{-1}. Satisfactory results of elemental analysis for complex **1b** could not be obtained due to its extreme sensitivity toward air and moisture.

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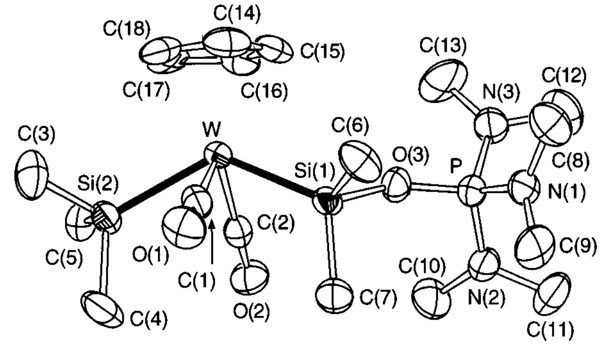
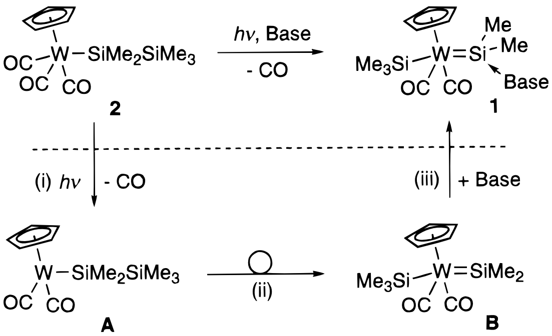


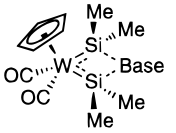
Figure 1. ORTEP drawing of **1a** with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and angles (deg): W−Si(1) 2.481(3), W−Si(2) 2.553(3), W−C(1) 1.927(10), W−C(2) 1.924(9), Si(1)−C(6) 1.876(10), Si(1)−C(7) 1.879(10), Si(1)−O(3) 1.774(6), Si(2)−C(3) 1.881(10), Si(2)−C(4) 1.890(11), Si(2)−C(5) 1.892(10), O(1)−C(1) 1.167(11), O(2)−C(2) 1.181(10), P−O(3) 1.515(6), Si(1)−W−Si(2) 128.76(8), C(2)−W−C(1) 99.7(4), C(6)−Si(1)−C(7) 105.1(5), C(6)−Si(1)-W 115.9(4), C(7)−Si(1)-W 118.4(3), O(3)−Si(1)−W 111.6(2), P−O(3)−Si(1) 147.2(4).

also formed. Complexes **1a** and **1b** were isolated as air-sensitive, pale yellow crystals in 20% yield. Complex **1a** was fully characterized by NMR, IR, and mass spectroscopy, elemental analysis, and X-ray crystal structure analysis.

Scheme 1



The X-ray crystal structure of **1a** (Figure 1)[15] revealed that the silylene ligand is *trans* to the silyl group (Si(1)−W−Si(2) 128.76(8)°), which contrasts with the *cis* geometry of the base-bridged bis(silylene)tungsten complexes $Cp(OC)_2W\{SiMe_2{\cdots}Base{\cdots}SiMe_2\}$ (**3**; Si−W−Si 62−64°).[8g] The *trans* geometry of **1a** is attributable to the steric repulsion between the silyl group and the HMPA-coordinated silylene ligand. A similar *trans* configuration was commonly observed in phosphine-substituted silyltungsten complexes of the type $CpW(CO)_2(PR_3)SiR'_3$.[17] The tungsten−silylene bond (W−Si(1) 2.481(3) Å) in **1a** is significantly shorter than that of the tungsten−silyl bond (W−Si(2) 2.553(3) Å) in the same complex and those of structurally similar alkylsilyltungsten complexes (2.53−2.63 Å).[17] The W−Si(1) bond distance is slightly shorter than those of the donor-bridged bis(silylene)tungsten complexes **3** (2.49−2.51 Å),[8g] however, slightly longer than that in a (perchlorodisilanyl)tungsten complex $(\eta\text{-}C_5Me_5)W(CO)_2(PMe_3)SiCl_2SiCl_3$ (2.469(2) Å).[17b] The Si(1)−O(3) distance (1.774(6) Å) is much longer than the usual Si−O single bonds (1.58−1.70 Å)[18] and in the range of the reported Si−O(HMPA) distance of the HMPA-coordinated silyleneiron and -chromium complexes (1.67−1.78 Å).[19] These structural data clearly demonstrate that the W−Si(1) and W−Si(2) bonds take on a double-bond character and a single-bond character, respectively, and the Si(1)−O(3) bond is regarded as a dative bond.



3: Base = NEt_2, OMe

The double-bond character of the tungsten−silylene bonding in **1** is also supported by the significant downfield shift of the ^{29}Si NMR signals as well as the large coupling constants between ^{29}Si and ^{183}W ($\delta = 92.5$ ppm ($^1J_{WSi} = 121$ Hz) for **1a** and $\delta = 144.7$ ppm ($^1J_{WSi} = 132$ Hz) for **1b**) compared to those of the silyl groups in **1** ($\delta = 18{-}19$ ppm, $^1J_{WSi} = 50{-}58$ Hz) and the structurally similar silyltungsten complexes ($\delta = -44{-}59$ ppm, $^1J_{WSi} = 41{-}65$ Hz).[17] Interestingly, the $^1J_{WSi}$ values for the silylene ligands in **1** are apparently larger than those of the donor-bridged bis(silylene)tungsten complexes **3** ($^1J_{WSi} = 91{-}100$ Hz).[8g] This indicates a higher bond order of the tungsten−silylene bonding in **1** than in **3**. In the latter complex, the formal bond order is expected to be 1.5.

The formation of **1** can be explained by a mechanism shown in Scheme 1: (i) Photochemical dissociation of a carbonyl ligand from **2** to give a 16-electron intermediate **A**, (ii) 1,2-shift of the silyl group to the coordinatively unsaturated tungsten to form base-free silyl(silylene)tungsten complex **B**, and (iii) coordination of a base to the electron-deficient silylene ligand to form **1**.

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(14) **1a**: A Pyrex sample tube (10 mm o.d., 8 mm i.d.) with a Teflon vacuum valve and a ground-glass joint was charged with a toluene solution (ca. 4 mL) of **2** (0.084 g, 0.18 mmol) and HMPA (0.033 mL, 0.18 mmol). The solution was subjected to three freeze−pump−thaw cycles and irradiated for 10 h. Volatiles were evaporated under high vacuum. The residue was extracted with hexane to remove insoluble black solids. The extract was concentrated until a small amount of crystals appeared in solution. Cooling the mixture at −30 °C afforded pale yellow crystals of **1a** (0.022 g, 0.036 mmol, 20%): ^1H NMR (300 MHz, C_6D_6, room temperature) δ 5.00 (s, 5H, Cp), 2.15 (d, 18H, $^3J_{PH} = 10.2$ Hz, HMPA), 1.04 (s, 9H, $SiMe_3$), 0.90 (s, 6H, $SiMe_2$); ^{13}C NMR (75.5 MHz, C_6D_6, room temperature) δ 228.3 (CO), 86.6 (Cp), 36.6 (d, $^2J_{PC} = 5.0$ Hz, HMPA), 12.4 ($SiMe_2$), 7.6 ($SiMe_3$); ^{29}Si NMR (59.6 MHz, C_6D_6, room temperature) δ 92.5 (d, $^2J_{PSi} = 28.8$ Hz, $^1J_{WSi} = 121$ Hz, $SiMe_2$), 18.6 (s, $^1J_{WSi} = 59$ Hz, $SiMe_3$); IR (C_6D_6) ν_{CO} 1857, 1778 cm^{-1}; MS (EI, 70 eV) *m*/*z* 436 (M^+ − HMPA, 5.49). Anal. Calcd for $C_{18}H_{38}O_3N_3PSi_2W$: C, 35.12; H, 6.22. Found: C, 35.19; H, 6.03.

(15) Crystal data for **1a**: $C_{18}H_{38}O_3N_3PSi_2W$, monoclinic, space group $P2_1/n$, $a = 9.236(4)$ Å, $b = 18.837(5)$ Å, $c = 15.007(2)$ Å, $\beta = 98.921(18)°$, $V = 2579.3(13)$ Å^3, $Z = 4$, $D_c = 1.585$ g/cm^3. The structure was solved by Patterson and Fourier transform methods and refined by full-matrix least-squares techniques on all F^2 data (5923 unique reflections) using SHELX-97.[16] R1 = 0.049 and wR2 = 0.105 for 3631 reflections with $I > 2.0\sigma(I)$.

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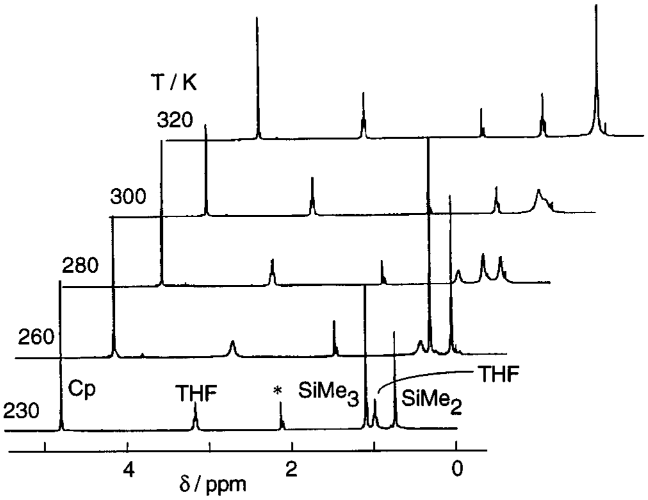
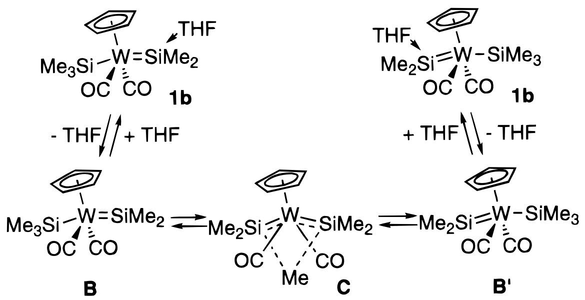


Figure 2. Variable-temperature ^{1}H NMR spectra (300 MHz) of **1b** measured in toluene-d_8. Asterisk (*) denotes $C_6D_5CD_2H$.

The THF-coordinated silyl(silylene)tungsten complex **1b** exhibits a dynamic process in solution. The ^{1}H NMR spectrum of the complex **1b** in toluene-d_8 at 230 K shows two singlet signals in the SiMe region at 0.71 and 1.04 ppm, which are assignable to the SiMe$_2$ and SiMe$_3$ ligands, respectively (Figure 2). As the temperature is raised from 230 K, the SiMe signals broaden, coalesce, and become a singlet peak at 320 K. The signals for the coordinated THF that appear at 0.95 and 3.15 ppm at 230 K also broaden at 260 K and become sharp signals at 280 K. These spectral changes clearly show that the intramolecular 1,3-methyl migration from the SiMe$_3$ group to the SiMe$_2$ ligand and exchange between the coordinated THF and a trace amount of free THF take place in the NMR time scale.

A proposed mechanism for the 1,3-methyl migration is given in Scheme 2: (i) Dissociation of the coordinated THF molecule from **1b** to give a base-free silyl(silylene)tungsten intermediate **B**, (ii) 1,3-methyl migration from the SiMe$_3$ group to the electron-deficient silylene ligand to afford intermediate **B′**, which proceeds most likely via a symmetric transition state (or intermediate) **C**, and (iii) recombination of a THF molecule with the silylene ligand in **B′** to reproduce **1b**. This mechanism is essentially the same as that proposed previously for the 1,3-methyl migration in the base-stabilized silyl(silylene)iron complex.[11]

Scheme 2



Interestingly, the HMPA-coordinated complex **1a**, in contrast to the THF-coordinated complex **1b**, does not show the dynamic behavior due to the 1,3-methyl migration under similar experimental conditions. This can be explained by the fact that the coordination of the HMPA molecule to the electron-deficient silylene ligand is much stronger than that of the THF molecule, which prevents the generation of the base-free silyl(silylene)tungsten intermediate **B**. Indeed, addition of HMPA to a solution of the THF-coordinated complex **1b** caused base substitution to produce the HMPA-coordinated complex **1a** almost quantitatively. The reactivity of the silyl(silylene)tungsten complexes can be controlled by the nature of the donor coordinated to the silylene ligand.

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Supporting Information Available: Text giving crystal structure determination details and tables giving crystal data, atomic coordinates and equivalent isotropic displacement parameters of non-hydrogen atoms, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **1a** (7 pages). Ordering information is given on any current masthead page.

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