Reversible 1,2-Migration of Aryl Groups on Silyl Ligands: Formation and Properties of Silylenetungsten Complexes Stabilized by an External Base

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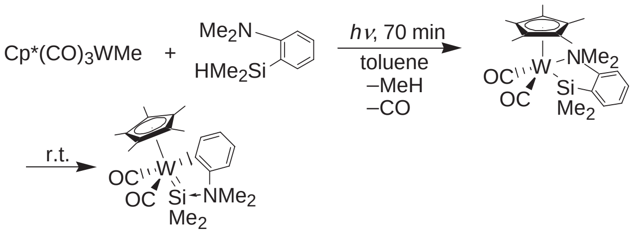
Irradiation of $Cp^*(CO)_3WMe$ and $HSiMe_2Ar$ ($Cp^* = \eta^5$-C_5Me_5, Ar = Ph, ^{p}Tol) in the presence of 4-(dimethylamino)pyridine (DMAP) led to the formation of base-stabilized silylene complex $Cp^*(CO)_2W(Ar)({=}SiMe_2{\cdot}DMAP)$ (**1**). On gentle heating, **1** was converted to the corresponding silyl complex $Cp^*(CO)_2(DMAP)WSiMe_2Ar$ (**2**) through the 1,2-migration of the aryl ligand to the silylene silicon. Irradiation of **2** reproduced the silylene complex **1**.

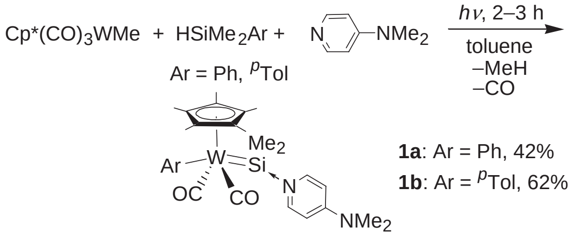
Coordinatively unsaturated transition-metal silyl complexes have been proposed as key intermediates in various metal-catalyzed transformations of organosilicon compounds. To gain insight into these complexes, we designed a Si,N-chelate ligand, (2-*N*,*N*-dimethylanilinyl)dimethylsilyl, which is expected to be hemilabile and readily opens a vacant site through decoordination of the dimethylamino side arm. Recently, we reported the photoreaction of $Cp^*(CO)_3WMe$ with *N*,*N*-dimethyl-2-(dimethylsilyl)aniline. This reaction proceeded through the transient formation of the Si,N-chelate complex, which was further converted to the base-stabilized silylene complex at room temperature through 1,2-migration of the aryl group (Scheme 1).[1] We now report that, in the non-chelate-type silyl complexes, this unusual 1,2-migration reaction proceeds *reversibly*.



Scheme 1.

Photolysis[2] of $Cp^*(CO)_3WMe$, $HSiMe_2Ar$ (Ar = Ph, ^{p}Tol), and 4-(dimethylamino)pyridine (DMAP) in toluene gave the external base-stabilized silylene complexes **1a** and **1b** in 42% and 62% yields, respectively (Eq 1).[3]

Recrystallization of **1a** from toluene at −16 °C yielded yellow crystals that were suitable for X-ray crystal structure analysis.[4] A molecular structure of **1a** is shown in Figure 1. Complex **1a** adopts a four-legged piano-stool geometry: the tungsten center possesses one Cp*, two carbonyl, one phenyl, and one silylene ligands, in which the phenyl and silylene ligands are located at the trans-positions. The DMAP molecule is coordinated to the silylene ligand with the lone pair of the nitrogen atom. The dative bond character is reflected in the significantly long distance of the Si–N1 bond (1.924(17) Å) compared to those of the normal Si–N covalent bonds (1.70–1.76 Å). The W–Si bond distance (2.511(5) Å) is slightly shorter than those of the silyltungsten complexes (2.53–2.63 Å)[5] and comparable to those of the base-stabilized silylenetungsten complexes (2.45–2.51 Å).[1,6] The sum of the bond angles around Si, excluding the nitrogen atom, is 343.3°, which is intermediate between the tetrahedral (329°) and trigonal (360°) values and is characteristic of those in the base-stabilized silylene complexes.[7]



(1)

The ^{29}Si NMR signals of **1a** (86.7 ppm) and **1b** (86.5 ppm) are significantly downfield-shifted compared with those of usual silyltungsten complexes (0–70 ppm)[7] and comparable to those of base-stabilized silylenetungsten complexes.[7]

1,2-Migration of an aryl group similar to the reaction in Eq 1 has been previously reported by Burger and Bergman for the cationic iridium complexes $[Cp^*(PMe_3)IrSiPhR_2](OTf)$ (R = Me or Ph) to give $Cp^*(PMe_3)IrPh(SiR_2OTf)$.[8]

Importantly, in our system, the 1,2-migration of the aryl group is reversible between the silyl and silylene complexes: Heating **1** at 55 °C for 11 h led to the complete disappearance of **1** to form the silyl complex **2** (Eq 2).[9] Apparently, silyltungsten complexes **2** are thermodynamically more stable than the

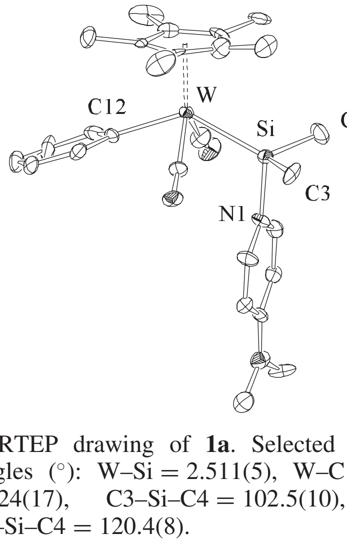
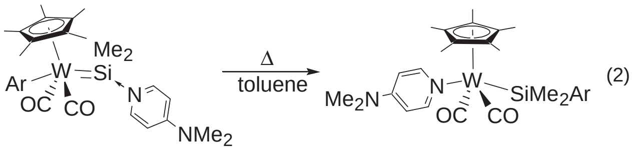


Figure 1. ORTEP drawing of **1a**. Selected bond distances (Å) and angles (°): W–Si = 2.511(5), W–C12 = 2.227(18), Si–N1 = 1.924(17), C3–Si–C4 = 102.5(10), W–Si–C3 = 120.4(6), W–Si–C4 = 120.4(8).

silylenetungsten complexes **1**. The activation parameters for the conversion of **1a** to **2a** are $\Delta H^{\ddagger} = 155(3)\,\mathrm{kJ\,mol^{-1}}$, $\Delta S^{\ddagger} = 152(9)\,\mathrm{J\,K^{-1}\,mol^{-1}}$, and $\Delta G^{\ddagger}_{298} = 110(6)\,\mathrm{kJ\,mol^{-1}}$.[10] The very large positive value for entropy of activation implies that this reaction proceeds through a dissociative mechanism.



(2)

1a: Ar = Ph
1b: Ar = ^{p}Tol

2a: Ar = Ph, 89%
2b: Ar = ^{p}Tol, 76%

A possible mechanism for the thermal isomerization in Eq 2 would start with dissociation of DMAP in **1**. The resulting base-free silylene complex undergoes 1,2-migration of the aryl group, and final coordination of DMAP to the tungsten center gives **2**. Although the 1,2-migration of an alkyl or aryl ligand to the silylene silicon atom has been proposed in some iridium[11,12] and platinum[13] systems, the reaction in Eq 2 represents the first example of the reaction in which the isolated silylene complex is converted to the silyl complex through 1,2-migration of an organic group.

Recrystallization of **2b** from toluene at room temperature yielded yellow crystals suitable for X-ray crystal structure analysis.[4] A molecular structure of **2b** is shown in Figure 2. Complex **2b** adopts a four-legged piano-stool geometry: the tungsten center possesses one Cp*, two carbonyl, one DMAP, and one silyl ligands. The *p*-tolyl group is located on the silyl silicon atom. The W–Si bond distance (2.617(3) Å) is longer than that in **1a** and lies in the normal range expected for tungsten-silicon single bond (2.53–2.63 Å).[5]

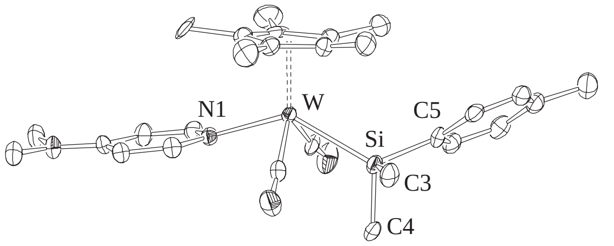
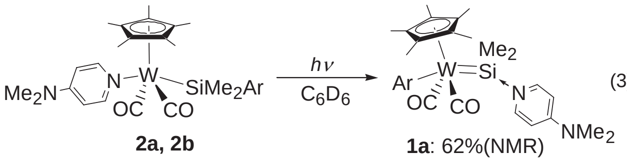


Figure 2. ORTEP drawing of **2b**. Selected bond distances (Å) and angles (°): W–Si = 2.617(3), W–N1 = 2.244(8), C3–Si–C4 = 102.9(6), C3–Si–C5 = 102.9(5), C4–Si–C5 = 103.8(5), W–Si–C3 = 116.3(4), W–Si–C4 = 111.6(3), W–Si–C5 = 117.6(3).

Irradiation[2] of the silyl complexes **2** reproduced the silylene complexes **1** in 62% (**1a**) and 64% (**1b**) NMR yields (Eq 3). The isomerization proceeded to completion within 3 min. A plausible mechanism for this photochemical isomerization involves photoinduced dissociation of the DMAP ligand in **2**, followed by the 1,2-migration of the aryl group and recoordination of DMAP to the silylene silicon atom. However, an alternative mechanism starting from photoinduced dissociation of a CO ligand can not be ruled out.



(3)

2a, 2b

1a: 62%(NMR)
1b: 64%(NMR)

In conclusion, for the first time, the reversible isomerization between the aryl(silylene) complex and arylsilyl complex via 1,2-aryl migration has been directly observed. In the photostationary state, silylene complexes **1** are predominant, whereas silyl complexes **2** are thermodynamically more stable than **1**.

References and Notes

1 M. Okazaki, E. Suzuki, N. Miyajima, H. Tobita, and H. Ogino, *Organometallics*, **22**, 4633 (2003).

2 A 450 W medium-pressure Hg lamp was used as a light source.

3 **1a**: ^{1}H NMR (300 MHz, C_6D_6) δ 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*-Ar-H), 7.33 (t, $J = 7.3$ Hz, 2H, *m*-Ar-H), 8.08 (m, 2H, *o*-Ar-H), 8.58 (m, 2H, py-H), ^{29}Si{^{1}H} NMR (59.6 MHz, C_6D_6) δ 86.7 ($J_{\mathrm{W-Si}} = 71$ Hz), IR (C_6D_6) 1784, 1869 cm^{-1} (ν_{CO}).

4 The crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC Nos. 270014–270015).

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9 **2a**: ^{1}H NMR (300 MHz, C_6D_6) δ 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*-Ar-H), 7.39 (t, $J = 7.4$ Hz, 2H, *m*-Ar-H), 8.24 (m, 2H, *o*-Ar-H), 8.34 (m, 2H, py-H), ^{29}Si{^{1}H} NMR (59.6 MHz, C_6D_6) δ 15.8 ($J_{\mathrm{W-Si}} = 31$ Hz), IR (C_6D_6) 1790, 1876 cm^{-1} (ν_{CO}).

10 The rate constants for isomerization of **1a** to **2a** at various temperatures are $1.18(2) \times 10^{-6}\,\mathrm{s^{-1}}$ (303 K), $9.8(4) \times 10^{-6}\,\mathrm{s^{-1}}$ (313 K), $1.96(6) \times 10^{-5}\,\mathrm{s^{-1}}$ (318 K), $4.82(6) \times 10^{-5}\,\mathrm{s^{-1}}$ (323 K), and $1.46(5) \times 10^{-4}\,\mathrm{s^{-1}}$ (328 K).

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