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# Facile Isomerization of a Tungsten Silyl Complex to a Base-Stabilized Silylene Complex via 1,2-Migration of an Aryl Group

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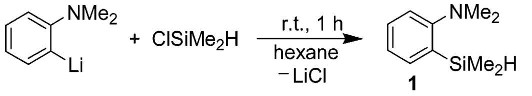
*Summary: Irradiation of Cp*(CO)$_3$WMe in the presence of N,N-dimethyl-2-(dimethylsilyl)aniline led to the intermediate formation of Cp*(CO)$_2$W{$\kappa^2$(Si,N)-Me$_2$N(o-C$_6$H$_4$SiMe$_2$)} (**3**), which was converted to the base-stabilized silylene complex Cp*(CO)$_2$W{$\kappa^2$(Si,C)-SiMe$_2$-NMe$_2$(o-C$_6$H$_4$)} (**2**) through 1,2-migration of the aryl group.*

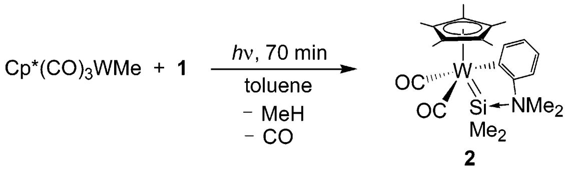
Transition-metal silyl complexes have been proposed as intermediates in various metal-catalyzed transformations of organosilicon compounds.[1] Although the syntheses and reactivities of various silyl complexes have been explored for decades, only scattered reports are available for coordinatively unsaturated silyl complexes.[2] To gain insight into these complexes, we designed a novel Si,N-chelate ligand, (2-*N*,*N*-dimethylanilinyl)dimethylsilyl, which is expected to be hemilabile in low-oxidation-state, electron-rich systems by reversible coordination of the nitrogen donor.[3] This paper reports on the reaction between Cp*(CO)$_3$WMe and *N*,*N*-dimethyl-2-(dimethylsilyl)aniline (**1**), resulting in the formation of Cp*(CO)$_2$W{$\kappa^2$(*Si*,*N*)-Me$_2$N(*o*-C$_6$H$_4$-SiMe$_2$)} (**3**). Subsequent rearrangement proceeded smoothly at room temperature to afford a base-stabilized silylene complex, Cp*(CO)$_2$W{$\kappa^2$(*Si*,*C*)-SiMe$_2$NMe$_2$-(*o*-C$_6$H$_4$)} (**2**), via 1,2-migration of the aryl group. To the best of our knowledge, complex **2** is the first silylene complex formed from a neutral silyl complex through 1,2-migration of an organic substituent. From a cationic complex, the same type of migration process has been previously reported by Burger and Bergman for the iridium complex [Cp*(PMe$_3$)IrSiR$_3$](OTf) to give Cp*-(PMe$_3$)IrR(SiR$_2$OTf).[4]

The ligand precursor **1** was synthesized by reacting ortho-lithiated *N*,*N*-dimethylaniline with chlorodimethylsilane (eq 1). From the reaction mixture, **1** was separated by silica gel column chromatography (10:1 hexanes−ether) as a colorless liquid in 28% yield.[5]



(1)

A solution of Cp*(CO)$_3$WMe and **1** in toluene was irradiated using a 450 W medium-pressure Hg lamp. During the photolysis for 70 min, the color of the solution turned from light yellow to brown. After the solution was allowed to stand at room temperature for a few hours, the reaction mixture was evaporated to dryness and the residual solid was washed with hexane to give **2** in 76% yield (eq 2).[6] Under these conditions, however, the expected Si,N-chelate complex Cp*(CO)$_2$W-



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[5] Synthesis of *N*,*N*-dimethyl-2-(dimethylsilyl)aniline (**1**): to a solution of *N*,*N*-dimethylaniline (24.2 g, 200 mmol) in hexane (60 mL) was added dropwise a hexane solution of *n*-BuLi (1.67 M in hexane, 157 mL, 262 mmol) at room temperature. Then, the mixture was stirred at 90 °C for 20 h to yield the ortho-lithiated compound as a yellow suspension. The suspension was cooled to room temperature and was added dropwise to a cold solution (0 °C) of chlorodimethylsilane (27.0 g, 286 mmol) in hexane (20 mL). After it was stirred for 1 h at room temperature, the reaction mixture was hydrolyzed with water (200 mL). The organic layer was separated from the aqueous layer, and the latter was extracted using hexane (2 × 100 mL). The combined organic extracts were washed first with water (2 × 200 mL) and then with saturated aqueous NaCl, dried with MgSO$_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography (10:1 hexanes−ether) to afford the pure product (10.1 g, 28% yield). $^1$H NMR (300 MHz, C$_6$D$_6$): $\delta$ 0.38 (d, $J = 3.7$ Hz, 6H, SiMe$_2$), 2.45 (s, 6H, NMe$_2$), 4.84 (septet, $J = 3.7$ Hz, 1H, SiH), 6.98−7.06 (m, 2H, aryl), 7.22 (t, $J = 7.3$ Hz, 1H, aryl), 7.53 (d, $J = 7.3$ Hz, 1H, aryl). $^{13}$C{$^1$H} NMR (75.5 MHz, C$_6$D$_6$): $\delta$ −3.0 (SiMe$_2$), 46.3 (NMe$_2$), 120.7, 124.9, 131.0, 135.2, 136.1, 161.1 (aryl). $^{29}$Si{$^1$H} NMR (59.6 MHz, C$_6$D$_6$): $\delta$ −20.6. EIMS (70 eV): *m*/*z* 179 (M$^+$, 85), 164 (M$^+$ − Me, 100), 149 (M$^+$ − Me$_2$, 57), 120 (M$^+$ − SiMe$_2$H, 68). IR (NaCl): 2123 cm$^{-1}$ ($\nu_{SiH}$). Anal. Calcd for C$_{10}$H$_{17}$NSi: C, 66.97; H, 9.55; N, 7.81. Found: C, 66.91; H, 9.43; N, 7.94.

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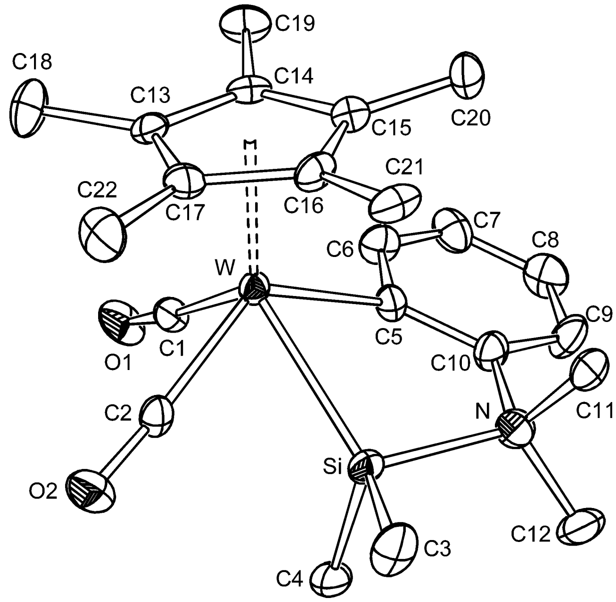

**Figure 1.** Molecular structure of **2**. Selected bond distances (Å) and angles (deg): W−Si = 2.487(3), W−C1 = 1.937(9), W−C2 = 1.943(8), W−C5 = 2.263(8), Si−N = 1.925(8); Si1−W−C1 = 105.8(3), Si−W−C2 = 68.2(3), Si−W−C5 = 68.8(2), C1−W−C2 = 78.3(3), C1−W−C5 = 81.7(4), C2−W−C5 = 124.7(3), W−Si−N = 105.9(2), W−Si−C3 = 123.3(3), W−Si−C4 = 116.1(3), N−Si−C3 = 102.7(4), N−Si−C4 = 100.7(4), C3−Si−C4 = 105.0(5).

{$\kappa^2$(*Si*,*N*)-$Me_2N(o\text{-}C_6H_4SiMe_2)$} (**3**) (vide infra) was not obtained at all. Recrystallization of **2** from benzene at room temperature yielded orange crystals that were suitable for X-ray crystal structure analysis.[7] As shown in Figure 1, complex **2** adopts a four-legged piano-stool geometry: the tungsten center possesses one Cp*, two carbonyl, and one $\kappa^2$(Si,C)-bidentate ligand. The W−C5 bond distance is 2.263(8) Å and is within the normal range of W−C(aryl) bond distances (2.16−2.33 Å).[8] The W−Si bond distance is 2.487(3) Å, which is significantly shorter than that of a typical tungsten−silicon single bond (2.53−2.63 Å)[1] but is comparable to those of the base-stabilized silylenetungsten complexes (2.45−2.51 Å).[9,10] The Si−N distance of 1.925(8) Å is considerably longer than that of normal Si−N covalent bonds (1.70−1.76 Å).[11] The sum of the bond angles around Si, excluding the nitrogen atom, is 344.4°, which is intermediate between the tetrahedral (329°) and trigonal (360°) values and is characteristic of those in the base-stabilized silylene complexes.

The unsaturated nature of the tungsten−silicon bond is also reflected in the significant downfield shift of the $^{29}$Si NMR signal as well as a large coupling constant between $^{29}$Si and $^{183}$W (115.0 ppm, $J_{Si-W}$ = 103 Hz) compared with those for previously reported silyltungsten complexes[1] and **3** (vide infra) (0−70 ppm, $J_{Si-W}$ = 42−64 Hz).

In an attempt to observe the intermediate, we monitored the photoreaction between $Cp^*(CO)_3WMe$ and **1** in benzene-$d_6$ using NMR spectroscopy. After photolysis for 6 min, 70% of $Cp^*(CO)_3WMe$ was consumed with the formation of **2** and the Si,N-chelate complex **3**[12] in a 1:1 molar ratio. Prolonged photolysis resulted in the disappearance of **3** to afford **2** in 68% yield. The reaction of **1** and $Cp^*(CO)_2(NCCD_3)WMe$, which was freshly prepared by irradiation of $Cp^*(CO)_3WMe$ in acetonitrile-$d_3$,[10] was also monitored at room temperature. After the reactants were mixed, the instantaneous formation of **2** and **3** in a 1:1 molar ratio was observed. At room temperature, complex **3** was thermally unstable and was almost quantitatively converted to **2** within 80 min. By NMR spectroscopy, the yield of **2** was estimated to be 86% based on $Cp^*(CO)_3WMe$.

The $^1$H NMR spectrum of **3** exhibits four peaks assignable to chemically inequivalent methyl groups ($\delta$ 0.77 and 1.07 ($SiMe_2$), $\delta$ 2.60 and 2.93 ($NMe_2$)). The chemical shift and the coupling constant observed in the $^{29}$Si{$^1$H} NMR ($\delta$ 33.5 ($J_{Si-W}$ = 56 Hz)) are consistent with those for silyltungsten complexes.[1] In the IR spectrum, the CO stretching vibrations were observed at 1807 and 1888 cm$^{-1}$.

A plausible mechanism for the formation of **2** and **3** is illustrated in Scheme 1. The coordinatively unsaturated complex [$Cp^*(CO)_2WMe$], which is generated by dissociation of one carbonyl ligand, undergoes oxidative addition of **1** at the Si−H bond. The resulting hydrido methyl silyl complex **A** releases methane by reductive elimination and then ligates the intramolecular nitrogen atom to give **3** as a kinetically favorable product. Complex **3**, in which the Si,N-chelate ligand is hemilabile through the reversible coordination/dissociation of the nitrogen atom, functions as a masked, coordinatively unsaturated silyl complex. The transient 16e silyl complex **B** undergoes 1,2-aryl migration followed by coordination of a nitrogen atom to the silylene ligand, to give the donor-stabilized silylene complex **2** as a thermodynamically favorable product.

Ruthenium and osmium complexes with a Si,P-chelate ligand, $\kappa^2$(*Si*,*P*)-$SiMe_2(o\text{-}C_6H_4PPh_2)$, have been

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(6) Synthesis of $Cp^*(CO)_2W${$\kappa^2$(*Si*,*C*)-$SiMe_2NMe_2(o\text{-}C_6H_4)$} (**2**): a toluene solution (7 mL) of $Cp^*(CO)_3WMe$ (151 mg, 0.36 mmol) and **1** (71 mg, 0.40 mmol) in a sealed Pyrex tube (12 mm o.d.) was irradiated with a 450 W medium-pressure Hg lamp for 70 min at 5 °C. After the solution was allowed to stand at room temperature for a few hours, the reaction mixture was transferred into a round-bottomed flask and evaporated to dryness. The residue was washed with hexane to give analytically pure **2** (151 mg) in 76% yield. $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 0.13, 0.63 (s, 3H × 2, $SiMe_2$), 1.92 (s, 15H, Cp*), 2.05, 2.25 (s, 3H × 2, $NMe_2$), 6.43, 6.83, 6.99, 7.83 (m, 1H × 4, aryl). $^{13}$C NMR (75.5 MHz, $C_6D_6$): $\delta$ 2.8, 3.5 ($SiMe_2$), 11.6 ($C_5\mathit{Me}_5$), 45.2, 49.5 ($NMe_2$), 100.9 ($\mathit{C}_5Me_5$), 116.2, 122.9, 126.3, 147.6, 154.0, 154.8 (aryl), 236.2, 241.0 (CO). $^{29}$Si NMR (59.6 MHz, $C_6D_6$): $\delta$ 115.0 ($J_{W-Si}$ = 103 Hz). EIMS (70 eV): *m/z* 553 ($M^+$, 37), 178 ([$o\text{-}SiMe_2(NMe_2)C_6H_4$]$^+$, 100). IR ($C_6D_6$): 1901, 1807 cm$^{-1}$ ($\nu_{CO}$). Anal. Calcd for $C_{22}H_{31}NO_2SiW$: C, 47.75; H, 5.65; N, 2.53. Found: C, 47.74; H, 5.53; N, 2.46.

(7) Crystal data for **2**: $C_{22}H_{31}NO_2SiW$, $M$ = 553.43, monoclinic, *Cc* (No. 9), $a$ = 10.610(1) Å, $b$ = 15.180(1) Å, $c$ = 13.4861(9) Å, $\beta$ = 94.782(5)°, $V$ = 2164.6(3), $D_c$ = 1.698 g cm$^{-3}$, $Z$ = 4, $T$ = 150 K, Mo K$\alpha$ ($\lambda$ = 0.710 69 Å), $\mu$ = 54.15 cm$^{-1}$, 9325 collected reflections, 2473 unique reflections ($R_{int}$ = 0.092), R1 = 0.033 ($I > 2.0\sigma(I)$), wR2 = 0.063, $R_w$ = 0.080 (all data).

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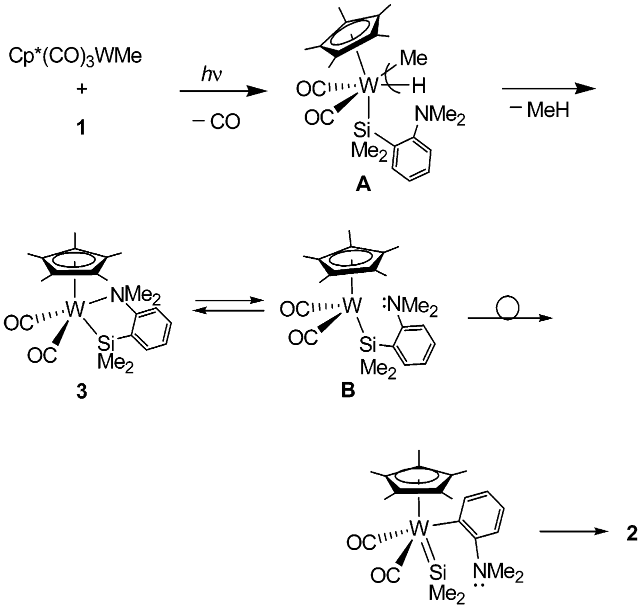
(12) Data for $Cp^*(CO)_2W${$\kappa^2$(*Si*,*N*)-$Me_2N(o\text{-}C_6H_4SiMe_2)$} (**3**) are as follows. $^1$H NMR (300 MHz, toluene-$d_8$, 253 K): $\delta$ 0.77, 1.07 (s, 3H × 2, $SiMe_2$), 1.53 (s, 15H, Cp*), 2.60, 2.93 (s, 3H × 2, $NMe_2$), 6.43 (m, 1H, aryl), 6.70−6.82 (m, 2H, aryl), 7.39 (m, 1H, aryl). $^{13}$C NMR (75.5 MHz, toluene-$d_8$, 253 K): $\delta$ 0.9, 8.6 ($SiMe_2$), 11.1 ($C_5\mathit{Me}_5$), 56.9, 67.7 ($NMe_2$), 101.3 ($\mathit{C}_5Me_5$), 113.4, 125.5, 126.8, 134.3, 146.3, 164.0 (aryl), 235.7, 248.4 (CO). $^{29}$Si NMR (59.6 MHz, toluene-$d_8$, 253 K): $\delta$ 33.5 ($J_{W-Si}$ = 56 Hz). IR ($C_6D_6$) 1888, 1807 cm$^{-1}$ ($\nu_{CO}$).

**Scheme 1. Plausible Formation Mechanism of 2 and 3**



synthesized as a thermally stable form.[13] The difference of the products between the Si,N- and Si,P-systems can be rationalized as follows. (i) Coordination of the nitrogen atom to the low-oxidation-state metal center is weaker than that of the phosphorus atom. (ii) The N-donor can stabilize the silylene complex by its coordination to the silicon atom more effectively than the P-donor.

It is reasonable to suggest that the 1,2-migration of the organic group in the silyl complex results in the formation of the silylene complex. This type of process has been previously reported for the transformation of transition-metal alkyl complexes to alkylidene complexes.[14] In the case of the germyl complex, Berry et al. proposed a mechanism to explain the ruthenium-mediated demethanative coupling of $HGeMe_3$, which involves an α-Me migration on $Ru(PMe_3)_4(GeMe_3)_2$ to generate $RuMe(PMe_3)_3(GeMe_2)(GeMe_3)$.[15] For silyl complexes, besides the example of cationic complexes mentioned in the introduction, the reverse pathway, i.e., 1,2-alkyl migration from the metal to the silylene silicon, has been reported by several groups.[16]

In conclusion, we demonstrated that the hemilabile Si,N-chelate ligand is suitable for investigation of the reactivity of coordinatively unsaturated silyl complexes. We directly observed, for the first time, the formation of the silylene complex via 1,2-aryl migration on a neutral silyl complex.

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**Supporting Information Available:** Text giving experimental details for the synthesis and characterization of all compounds and full details of the crystal structure analysis as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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