The First Resonance Hybrid of Silyl–Carbene and Pyridyl–Silylene Complexes: Formation by Aryl C–H Bond Activation of DMAP [4-(Dimethylamino)pyridine] on a Silylene Complex

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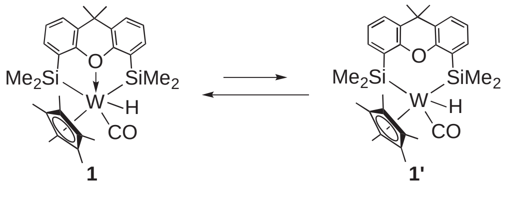
Treatment of a tungsten bis(silyl) complex Cp*W{κ^3-(*Si*,*Si*,*O*)-xantsil}(CO)(H) [xantsil = (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl)] with 4-(dimethylamino)pyridine (DMAP) causes ortho-metallation in a DMAP-stabilized silylene complex that is generated from the bis(silyl) complex through silicon-to-tungsten 1,2-methyl migration and methane elimination. Resulting W–Si–N–C four-membered metallacycle Cp*W[κ^3(*Si*,*Si*,*C*)-(SiMe$_2$){SiMe(NC$_5$H$_3$NMe$_2$)}-(C$_{15}$H$_{12}$O)](CO)(H) can be regarded as the resonance hybrid of silyl–carbene and pyridyl–silylene complexes.

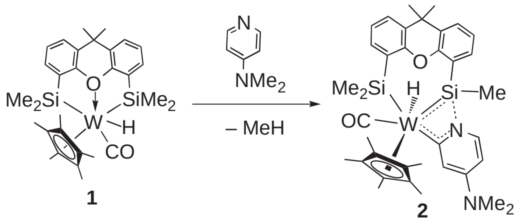
Transition-metal silylene complexes have attracted much attention because of their unique reactivity based on the highly polarized $M^{\delta-}{=}Si^{\delta+}$ bond and dynamic behaviors.[1] An important aspect of silylene complexes that stimulates the application studies on catalytic reactions is their easy formation from silyl complexes via 1,2-group migration reactions.[2] It is well known that silylene complexes can be prepared by 1,2-migration of a silyl group or a hydrogen atom to a coordinatively unsaturated metal center. A similar 1,2-migration of an aryl or alkyl group has also been reported by Burger and Bergman on cationic silyliridium complexes.[3] We recently demonstrated that 1,2-aryl migration is available for the synthesis of base-stabilized neutral silylenetungsten complexes Cp*W(CO)$_2$(Ar)(=SiMe$_2$·DMAP).[4]

During our research on the chemistry of tungsten complex **1** having a xantsil ligand, i.e. a tridentate Si,O,Si-chelate ligand, we found that the oxygen coordination is labile and facile cleavage of the W–O bond generates a coordinatively unsaturated bis(silyl) intermediate **1′** (Eq 1).[5] In the reaction of **1** with ^{t}BuCN, the nitrile was coordinated to the unsaturated tungsten center of **1′** and subsequent silyl migration to the nitrogen atom yielded an η^2-iminoacyl complex.[5] We now report that the reaction of **1** with DMAP gives rise to 1,2-migration of a methyl group on a silicon of the xantsil ligand to the tungsten center, which finally affords a new W–Si–N–C four-membered metallacycle.



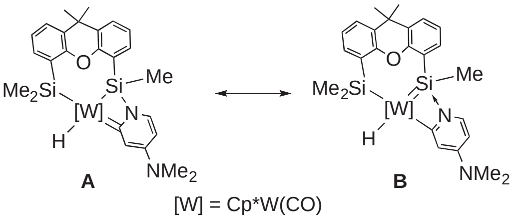
(1)

Treatment of the tungsten κ^3(*Si*,*Si*,*O*)-xantsil complex **1** with DMAP in toluene at room temperature for 1.5 days afforded a W–Si–N–C four-membered metallacycle **2** in 86% isolated yield (Eq 2).[6,7] During the course of this reaction in C$_6$D$_6$, the signals of methane (δ 0.15) and some unidentified intermediates were observed by ^{1}H NMR. The product is characterized by analytical and spectroscopic methods (see Supporting Information).[6] The ^{1}H NMR spectrum in C$_6$D$_6$ solution exhibits only three inequivalent SiMe signals at δ 1.46, 1.35, and 1.08 in 1:1:1 intensity ratio, indicating that one methyl group on the silyl ligand of **1** is lost through methane formation. The ^{29}Si{^{1}H} NMR spectrum shows two signals [δ 8.1 ($^1J_{WSi}$ = 84 Hz) and 1.9 ($^1J_{WSi}$ = 71 Hz)]. The former signal is assignable to the ring silicon based on the ^{1}H–^{29}Si COLOC NMR spectrum in which the former signal shows a cross-peak with only one SiMe proton resonance (δ 1.35). These ^{29}Si NMR chemical shifts, which are comparable to that of xantsil complex Cp*W{κ^2(*Si*,*Si*)-xantsil}(CO)$_2$(H) (δ 10.8),[5] are in the range of those for silyl ligands. A signal at δ 186.9 in the ^{13}C{^{1}H} NMR spectrum can be assigned to the carbon of the W–Si–N–C four-membered ring bearing partial carbene character, but this is fairly highfield-shifted compared to that of related 1,2-dihydropyridin-2-ylidene tungsten complexes (δ 211–215).[8] This implies a significant contribution of the pyridyl–silylene canonical structure **B** in Scheme 1 (vide infra).



(2)

The molecular structure of **2** having a unique W–Si–N–C four-membered ring was determined by X-ray crystallography (Figure 1).[9] The W–Si1 bond [2.528(1) Å], which is shorter than the W–Si2 bond [2.595(1) Å], is slightly longer than those of donor-stabilized bis(silylene) complex CpW(CO)$_2$-{(SiMe$_2$)···NEt$_2$···(SiMe$_2$)} [2.502(2) and 2.501(2) Å] containing a related W–Si–N–Si four-memebered ring structure.[10] The Si1–N1 bond [1.832(4) Å] is longer than normal Si–N single bonds of aminosilyl complexes (1.70–1.78 Å),[11] while it is shorter than that of DMAP-stabilized silylenetungsten complex Cp*(CO)$_2$W(Ph)(=SiMe$_2$·DMAP) [1.924(17) Å].[4] The W–C1



Scheme 1. Canonical structures for complex **2**.

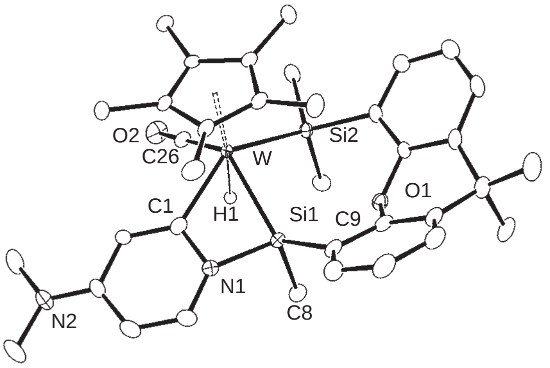


Figure 1. Molecular structure of **2**. Selected bond distances (Å) and angles (°): W–Si1 2.528(1), W–Si2 2.595(1), W–C1 2.195(4), W–C26 1.952(5), W–H1 1.72(7), Si1–N1 1.832(4), N1–C1 1.387(6), O2–C26 1.159(6), Si1–W–Si2 85.12(4), Si1–W–C1 61.6(1), Si2–W–C1 135.1(1), Si1–W–C26 125.6(1), Si2–W–C26 86.9(1), C1–W–C26 89.1(2), W–Si1–N1 85.3(1), W–Si1–C8 128.1(2), W–Si1–C9 122.8(1), W–C1–N1 111.6(3), Si1–N1–C1 97.4(3), C8–Si1–C9 103.0(2).

bond length [2.195(4) Å] is somewhat shorter than those of 1,2-dihydropyridin-2-ylidene tungsten complexes [2.287(12) and 2.277(5) Å][8] and comparable to those of Fischer-type carbene complexes having W–C–C–S and W–C–C–P four-membered rings [2.200(4) and 2.237(3) Å, respectively].[12] The sum of the bond angles between the three bonds around the Si1 atom except the N1–Si1 bond is 353.9(5)° that is located between the tetrahedral (329°) and trigonal (360°) valence angles. These X-ray and NMR data suggest that the structure of complex **2** can be described as a combination of two canonical structures **A** (carbene–silyl) and **B** (pyridyl–silylene) (Scheme 1).

Another unique structural feature of complex **2** is a possible hypervalent interaction of the ring silicon Si1 with the xanthene oxygen O1 located on the position trans to N1: the distance between Si1 and O1 is 2.693(3) Å, which is much shorter than the distance between Si2 and O1 [3.037(3) Å] as well as the sum of the van der Waals radii (3.4 Å), and the O1–Si1–N1 angle is 169.2(2)°.[13] This weak Si···O interaction is attributable to the geometrical constraints of the fused polycyclic structure and also donation of the oxygen lone pair to the electron-deficient silicon center due to the contribution of silylene complex structure **B**.

A plausible formation mechanism for **2** involves the initial dissociation of the labile oxygen ligand on **1** (see Eq 1) followed by 1,2-methyl migration to the tungsten center of **1′** and coordination of DMAP to the silylene center (Scheme 2). Reductive elimination of methane from silylene complex **C** generates a 16-electron metal center, which finally activates the ortho C–H bond of DMAP coordinated to the silylene ligand to give **2**.

In conclusion, we synthesized and characterized the first W–Si–N–C four-membered metallacycle **2** that can be regarded as the resonance hybrid of silyl–carbene and pyridyl–silylene complexes. A DMAP molecule was transformed into a N-heterocyclic bridging ligand during the formation of **2**, and the transformation was thought to be mediated by a metal–silylene intermediate generated by 1,2-methyl migration.[14]

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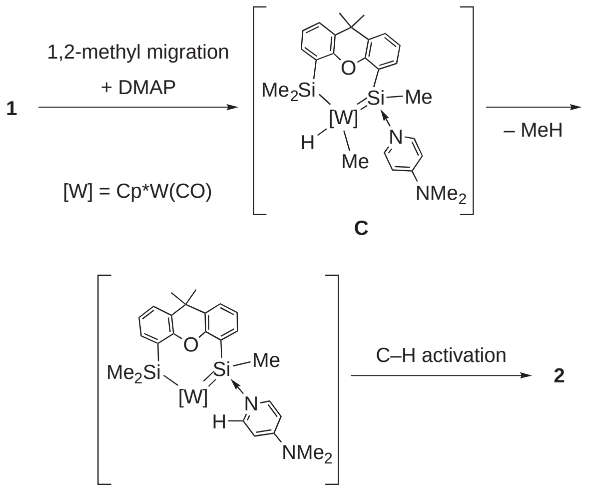

Scheme 2. A possible mechanism for the formation of **2**.

References and Notes

1 M. Okazaki, H. Tobita, H. Ogino, *Dalton Trans.* **2003**, 493, and references cited therein.

2 H. Ogino, *Chem. Rec.* **2002**, *2*, 291.

3 P. Burger, R. G. Bergman, *J. Am. Chem. Soc.* **1993**, *115*, 10462.

4 E. Suzuki, M. Okazaki, H. Tobita, *Chem. Lett.* **2005**, *34*, 1026.

5 R. Begum, T. Komuro, H. Tobita, *Chem. Commun.* **2006**, 432.

6 Supporting Information (experimental procedures and characterization data for **2**) is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

7 The NMR-tube reaction of **1** with pyridine in C_6D_6 afforded a complicated mixture of unidentified products.

8 R. Aumann, K. Roths, M. Grehl, *Synlett* **1993**, 669; R. Aumann, M. Kößmeier, K. Roths, R. Fröhlich, *Synlett* **1994**, 1041; R. Aumann, K. Roths, B. Jasper, R. Fröhlich, *Organometallics* **1996**, *15*, 1257.

9 Crystallographic data for **2**: $C_{36}H_{46}N_2O_2Si_2W$, $M_r = 778.78$, triclinic, space group $P\bar{1}$, $a = 10.2524(1)$, $b = 10.9538(4)$, $c = 15.4573(6)$ Å, $\alpha = 89.322(2)$, $\beta = 87.029(1)$, $\gamma = 77.363(2)°$, $V = 1691.57(9)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.529\,\mathrm{g\,cm^{-3}}$, 7690 unique reflections, $R1 = 0.031$ [$I > 2\sigma(I)$], $wR2 = 0.091$ (all data). Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-632455. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

10 K. Ueno, A. Masuko, H. Ogino, *Organometallics* **1997**, *16*, 5023.

11 T. Watanabe, H. Hashimoto, H. Tobita, *J. Am. Chem. Soc.* **2006**, *128*, 2176.

12 S. Cronje, G. R. Julius, E. Stander, C. Esterhuysen, H. G. Raubenheimer, *Inorg. Chim. Acta* **2005**, *358*, 1581.

13 D. Kost, I. Kalikhman, in *The Chemistry of Organic Silicon Compounds*, ed. by Z. Rappoport, Y. Apeloig, Wiley, New York, **1998**, Vol. 2, pp. 1339–1445; F. P. Boer, F. P. van Remoortere, *J. Am. Chem. Soc.* **1970**, *92*, 801; K. Dannappel, M. Schürmann, B. Costisella, K. Jurkschat, *Organometallics* **2005**, *24*, 1031.

14 A related conversion of pyridine derivatives into N-heterocyclic carbene ligands mediated by an iridium(III) complex has recently been reported: E. Alvarez, S. Conejero, M. Paneque, A. Petronilho, M. L. Poveda, O. Serrano, E. Carmona, *J. Am. Chem. Soc.* **2006**, *128*, 13060.

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