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Synthesis of a Base-Stabilized Silanone-Coordinated Complex by Oxygenation of a (Silyl)(silylene)tungsten Complex

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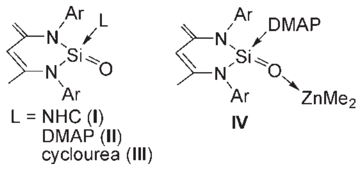
S *Supporting Information*

ABSTRACT: Base-stabilized silanone complex Cp*(OC)$_2$W(SiMe$_3$){O=SiMes$_2$(DMAP)} (**2**) was synthesized by the reaction of (silyl)(silylene)tungsten complex Cp*(OC)$_2$W(SiMe$_3$)(=SiMes$_2$) (**1**) with 1 equiv of pyridine-*N*-oxide (PNO) in the presence of 4-(dimethylamino)pyridine (DMAP). Further oxygenation of **2** with 3 equiv of PNO at 80 °C resulted in the formation of a W—O—Si—O—Si framework to give disiloxanoxy complex Cp*(O)$_2$W{OSiMes$_2$(OSiMe$_3$)} (**3**). Complex **3** was also obtained by the direct reaction of complex **1** with 4 equiv of PNO at 80 °C.

Ketones (R$_2$C=O) have been recognized as one of the most versatile building blocks for synthesis of a variety of organic molecules. On the other hand, silanones (R$_2$Si=O), a heavier congener of ketones, are unstable and readily oligomerized to give organopolysiloxanes (silicones) at ambient temperature.[1] Therefore, the peculiarity of the Si=O bond was revealed only by low-temperature spectroscopy.[2] The high reactivity of silanones is attributed to the strongly polarized Si=O bond, which is considered to have zwitterionic character with an electron-deficient Si$^+$ center and a negatively charged oxygen atom.[3] Driess and co-workers have recently stabilized and isolated silanones as Lewis base adducts, **I** (L = *N*-heterocyclic carbene (NHC)), **II** (L = 4-(dimethylamino)pyridine (DMAP)), and **III** (L = cycloourea), in which the electron-deficient Si$^+$ center is stabilized efficiently by coordination of a Lewis base L as well as delocalization of the nitrogen lone-pair electrons in the cyclic diamide substituent (Chart 1).[4] A silanone-coordinated Zn complex **IV**, which can be categorized as a Lewis base and acid adduct, was also prepared by addition of **II** to a Lewis acid, ZnMe$_2$ (Chart 1).[4f]

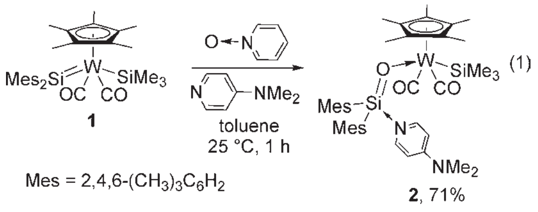
Coordination of silanones to transition metal fragments to form silanone complexes L$_n$M(O=SiR$_2$) (L$_n$M = transition metal fragment) should be a promising way to stabilize silanones.[5] A possible path to synthesis of silanone-coordinated complexes is oxygen addition to the M=Si bond of silylene transition metal complexes L$_n$M=SiR$_2$.[6] However, attempts to synthesize the silanone-coordinated complexes via the oxygen addition path have failed so far.[7] Corriu et al. reported that oxygenation of a silyleneiron complex by O$_2$ resulted in the formation of cyclotrisiloxane, which was produced by trimerization of transient silanones.[7a] Elimination of the silanone fragment to give cyclotrisiloxane (OSi^{i}Pr$_2$)$_3$ was also reported by Tilley et al. in the reaction of a cationic silylene complex [Cp*(Me$_3$P)$_2$Os(=Si^{i}Pr$_2$)]$^+$ (Cp* = η^5-C$_5$Me$_5$) with oxygenation reagents.[7b]

Chart 1



We have investigated the reactivity of (silyl)(silylene)tungsten and -molybdenum complexes Cp*(OC)$_2$M(SiMe$_3$)(=SiMes$_2$) (M = W (**1**), Mo; Mes = 2,4,6-(CH$_3$)$_3$C$_6$H$_2$)[8] and recently reported that the reaction of **1** with sulfur provided cyclic carbene compound Cp*(S)W{=C(SiMe$_3$)C(=O)OSiMes$_2$S}.[8b] This reaction is proposed to proceed via the initial formation of a silathione (R$_2$Si=S)-coordinated complex and gave the final product without loss of the silathione ligand.[8b] This result prompted us to investigate the reactivity of **1** with oxygenation reagents. In this paper, we report that the reaction of **1** with pyridine-*N*-oxide (PNO) in the presence of DMAP did not cause the silanone elimination but afforded DMAP-stabilized silanone complex Cp*(OC)$_2$W(SiMe$_3$){O=SiMes$_2$(DMAP)} (**2**). Further reaction of **2** with PNO resulted in the oxygenation and migration of the SiMe$_3$ group to form disiloxanoxy complex Cp*(O)$_2$W{OSiMes$_2$(OSiMe$_3$)} (**3**) as a final product.

Treatment of **1** with 1 equiv of PNO in the presence of DMAP in toluene at 25 °C for 1 h afforded DMAP-stabilized silanone-coordinated complex **2** with complete consumption of both **1** and PNO. Complex **2** was isolated as red crystals in 71% yield (eq 1). The elemental analysis data are consistent with the composition of complex **2**.



The structure of **2** was confirmed by crystal structure analysis (Figure 1). The tungsten atom is attached to a DMAP-stabilized silanone O=SiMes$_2$(DMAP), SiMe$_3$, Cp*, and two CO ligands. The long W···Si2 distance (3.639(2) Å) and the wide W—O3—Si2 angle (155.3(3)°) indicate no direct interaction between

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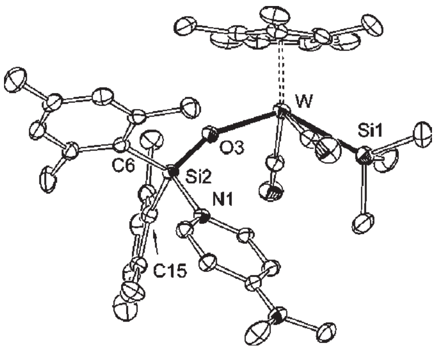


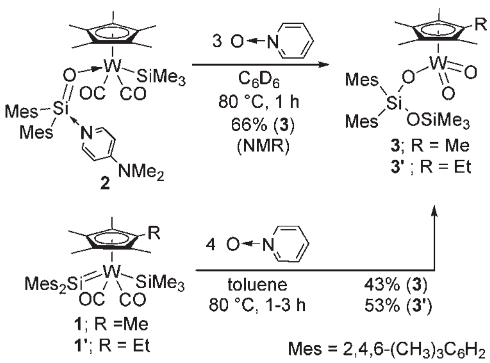
Figure 1. ORTEP drawing of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): W−Si1 2.625(2), W−O3 2.165(4), Si2−O3 1.558(4), Si2−N1 1.865(5), Si1−W−O3 134.81(12), W−O3−Si2 155.3(3), O3−Si2−C6 113.5(3), O3−Si2−C15 113.3(3), C6−Si2−C15 117.2(3).

W and Si2, i.e., η^1-coordination of the silanone ligand via the oxygen atom. This is also supported by the fact that the W−O3 bond distance (2.165(4) Å) is significantly longer than W−OSiR$_3$ single bonds (1.79−1.97 Å)[9] and slightly shorter than those of the η^1-coordinated O=CR$_2$ to tungsten (2.21−2.39 Å).[10] The structual parameters for the base-stabilized silanone ligand in **2** are comparable to those of the Driess's silanones **I**, **II**, and **III** and silanone zinc complex **IV**.[4] The Si2−O3 bond length (1.558(4) Å) is shorter than usual Si−O single bonds (1.60−1.66 Å),[11] comparable to those observed for **I** (1.541(2) Å),[4b] **II** (1.545(2) Å),[4e] **III** (1.532(2) Å),[4d] and **IV** (1.548(1) Å),[4f] and in the range of the theoretically calculated R$_2$Si=O bond lengths (1.50−1.60 Å).[1c,3c,5,12] The bond distance between the silanone silicon (Si2) and the coordinated DMAP nitrogen (N1) (1.865(5) Å) is also comparable to those in **II** (1.862(2) Å)[4e] and **IV** (1.848(2) Å)[4f] and much longer than usual Si−N single bonds (1.69−1.77 Å).[11] The sum of the three bond angles around Si2 except for the Si2−N1 bond is 344(1)°, which is between ideal sp^2 (360°) and sp^3 (327°) hybridizations.

Complex **2** shows two ^{29}Si NMR signals assignable to the DMAP-stabilized silanone ligand and the SiMe$_3$ group at −26 and 19 ppm, respectively. The former is significantly shifted to higher field than that of the silylene silicon atom in **1** (380 ppm)[13] and those of base-stabilized silylenetungsten complexes (49−148 ppm),[13−15] while the latter is within the usual chemical shift range for W−SiR$_3$ complexes (−3 to 29 ppm).[13,14,16] In the IR spectrum of **2**, two intense $\nu_{\mathrm{C=O}}$ bands were observed at 1857 and 1763 cm^{-1}, which are red-shifted about 30−60 cm^{-1} compared to those observed for **1** (1890 and 1828 cm^{-1}).[13] This red shift implies the stronger electron-donating character of the η^1-coordinated O=SiMes$_2$(DMAP) ligand in **2** than that of the silylene ligand SiMes$_2$ in **1** and implies the significant contribution of the strongly polarized form, Cp*(OC)$_2$W$^{\delta-}$(SiMe$_3$){OSiMes$_2$(DMAP$^{\delta+}$)}.

The silanone complex **2** is stable at ambient temperature but decomposes gradually at 50 °C (76% for 180 h) and rapidly at 80 °C (79% for 3 h) in C$_6$D$_6$ to give complex mixtures. In contrast to the thermolysis of **2**, oxygenation of silanone complex **2** took place quickly and relatively cleanly in the presence of 3 equiv of PNO in C$_6$D$_6$ at 80 °C for 1 h. This reaction proceeded with the construction of a W−O−Si−O−Si framework and the replacement of two CO with two oxo ligands to afford dioxo(disiloxanoxy)tungsten complex **3** in 66% NMR yield (Scheme 1). Complex **3** was also obtained by the direct reaction between **1** and 4 equiv of PNO in toluene at 80 °C for 3 h (Scheme 1). Elemental analysis supports the composition of **3**. The ^{29}Si NMR spectrum of **3** showed the resonances for Me$_3$Si and Mes$_2$Si at 11 and −34 ppm, respectively, which are comparable to those for the corresponding OSiMe$_3$ group (−5 to 25 ppm) and O−SiAr$_2$−O group (−40 to 0 ppm), respectively.[17] In the IR spectrum, two W=O stretching absorptions were observed at 899 and 954 cm^{-1}.[18] These spectroscopic data support the structure of **3** shown in Scheme 1. The structure of **3** is further established by crystal structure analysis of an η^5-C$_5$Me$_4$Et (Cp$^{*\mathrm{Et}}$) derivative of **3**, i.e., Cp$^{*\mathrm{Et}}$(O)$_2$W{OSiMes$_2$(OSiMe$_3$)} (**3′**) (Figure 2).

Scheme 1



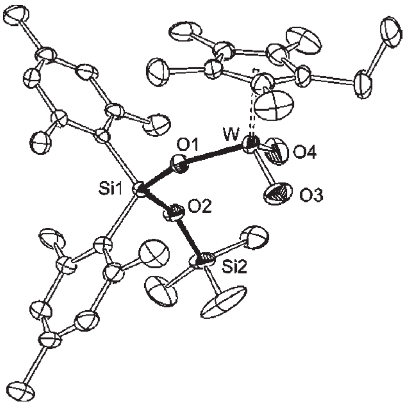


Figure 2. ORTEP drawing of **3′**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): W−O1 1.912(3), W−O3 1.724(4), W−O4 1.740(4), Si1−O1 1.638(3), Si1−O2 1.619(3), Si2−O2 1.638(3), O1−W−O3 103.59(18), O1−W−O4 106.04(17), O3−W−O4 105.7(3).

The W−O1 (1.912(3) Å) and Si−O (av. 1.632(3) Å) distances are within the usual range for W−OSiR$_3$ single bonds (1.79−1.97 Å)[9] and Si−O single bonds (1.60−1.66 Å),[11] respectively. The W=O3 and W=O4 bond distances (1.724(4) and 1.740(4) Å) are typical of those observed for bis(oxo) tungsten complexes (1.71−1.74 Å).[18a,19]

Complex **2** would be formed by oxygen addition to the W=Si bond in **1** to give a base-free silanone complex Cp*(OC)$_2$W(SiMe$_3$)(O=SiMes$_2$), followed by coordination of DMAP (or the resulting free pyridine, which is readily replaced by a more basic DMAP).[20] The mechanism of the transformation from **2** to disiloxanoxy complex **3** with PNO is still unclear. However, monitoring the reaction by ^{1}H NMR indicates that the reaction proceeds via the formation of PNO-coordinated silanone complex Cp*$(OC)_2W(SiMe_3)\{O{=}SiMes_2(PNO)\}$ (**A**), which is identified on the basis of the similarity of its ^{1}H NMR signals to those observed for **2**, except for the Lewis base fragment.[21] Further reactivity of silanone complex **2** and the mechanistic details of transformation of **2** to **3** are currently under investigation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, tables, figures, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Initial formation of DMAP-coordinated (silyl)(silylene) complex Cp*$(OC)_2W(SiMe_3)\{{=}SiMes_2(DMAP)\}$ followed by oxygenation is improbable since no spectral change was observed upon addition of DMAP to silylene complex **1**, probably due to the steric crowding by two Mes groups and the tungsten fragment.

(21) ^{1}H NMR data (300 MHz, C_6D_6) for complex **A** are as follow: δ/ppm 8.43 (m, 2H, PNO), 6.69 (s, 4H, *m*-H), 6.41 (m, 1H, PNO), 6.10 (m, 2H, PNO), 2.70−2.50 (bs, 12H, *o*-Me), 2.04 (s, 6H, *p*-Me), 1.93 (s, 15H, C_5Me_5), 0.89 (s, 9H, $SiMe_3$). For the data for complex **2**, see Supporting Information.