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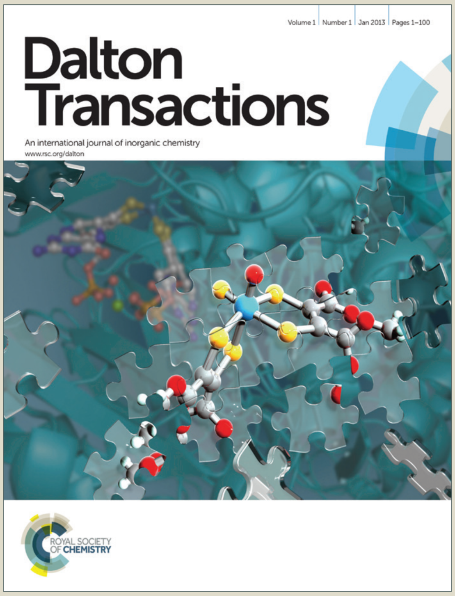

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Synthesis, Structures, and Reactivity of the Base-Stabilized Silanone Molybdenum Complexes†

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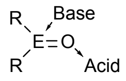
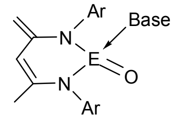
Base-stabilized silanone molybdenum complexes were synthesized by the oxygenation of the M=Si bond in the silyl(silylene)molybdenum complex with 1 eq of PNO in the presence of Lewis base L. PNO-coordinated silanone complex (L = PNO) was converted to *cis*-[Cp*(OC)$_2$Mo-{OSiMes$_2$(OSiMe$_3$)}(PMe$_3$)] in the presence of excess PMe$_3$.

Much interest has been concentrated on the investigation of heavier congeners of ketones $R_2E=O$ (E = Si, Ge, Sn, Pb) for decades.[1] Due to the highly polarized nature of the E=O bonds, such compounds are extremely reactive and readily oligomerized at ambient temperature. To isolate the $R_2E=O$ compounds as monomer units, it is essential to introduce sterically bulky substituents as R and a Lewis base on E (**A**, E = Si).[2,3] Driess and co-workers succeeded to isolate the first donor-stabilized silanones and germanones **B** utilizing bulky amido substituents as R on E.[4,5] Donor-stabilized silanone with alkyl substituents was also recently synthesized by Baceiredo and Kato et al.[6] Filippou et al. reported a unique L_nM-substituted silanone with a trigonal planar coordinated Si center.[7] Matsuo and Tamao et al. succeeded to isolate the first donor-free germanone (Eind)$_2$Ge=O (**I**) by oxygenation of the corresponding germylene (Eind)$_2$Ge with Me_3N-O in which the steric bulk of two Eind groups efficiently prevent the intermolecular oligomerization.[8]



A

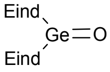


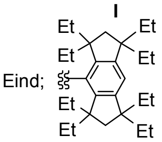
B

E = Si, Ge

Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$

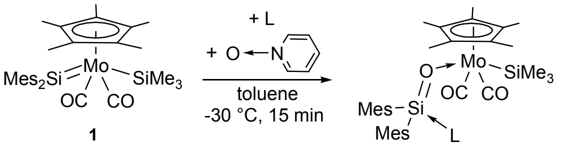
I





Coordination of $R_2E=O$ compounds to transition metal fragments to form $R_2E=O$-coordinated complexes could be an alternative strategy for stabilizing $R_2E=O$ compounds.[9,10] Driess and co-workers have reported synthesis of the first silanone-coordinated metal complex (metal: Zn) by the reaction of isolated donor-stabilized silanone **B** (E = Si) and Lewis acidic metal fragment $ZnMe_2$.[9] We have also reported synthesis and structure of the first silanone-coordinated tungsten complex [Cp*(OC)$_2$W(SiMe$_3$){O=SiMes$_2$(DMAP)}] (**II**, Cp* = η^5-C$_5$Me$_5$, Mes = 2,4,6-Me$_3$C$_6$H$_2$, DMAP = 4-(dimethylamino)pyridine).[10] Complex **II** was obtained by oxygenation of the W=Si bond in silyl(silylene) complex [Cp*(OC)$_2$W(SiMe$_3$)(=SiMes$_2$)] (**III**) with pyridine-*N*-oxide (PNO) in the presence of DMAP and isolated in 71% yield. The oxygenation reaction of the L_nM=Si bond in the silylene complexes would be applicable to the synthesis of a variety of the silanone complexes, however, no successful example has been reported so far except for **II**.[11] In this paper, we report synthesis of silanone Mo complexes [Cp*(OC)$_2$Mo(SiMe$_3$){O=SiMes$_2$(L)}] (L = DMAP (**2a**), PNO (**2b**)) via oxygenation of Mo=Si bond in silyl(silylene) complex [Cp*(OC)$_2$Mo(SiMe$_3$)(=SiMes$_2$)] (**1**). Preliminary investigations revealed that the reactivity of molybdenum complexes **2** is quite different from that of tungsten analogue **II**.

Reaction of silyl(silylene)molybdenum complex [Cp*(OC)$_2$Mo(SiMe$_3$)(=SiMes$_2$)] (**1**) with 1 equiv of PNO in the presence of DMAP in toluene at -30 °C for 15 min resulted in the complete consumption of **1**, PNO, and DMAP to afford DMAP-stabilized silanone-coordinated molybdenum complex [Cp*(OC)$_2$Mo(SiMe$_3$){O=SiMes$_2$(DMAP)}] (**2a**). Complex **2a** was isolated as orange crystals in 64% yield (eq 1). PNO-coordinated silanone complex [Cp*(OC)$_2$Mo(SiMe$_3$){O=SiMes$_2$(PNO)}] (**2b**) was also obtained by the reaction of **1** with 2 equiv of PNO under similar reaction conditions (eq 1). In this case, PNO functions as an oxygenation reagent to provide silanone ligand Mes$_2$Si=O and also as a Lewis base to stabilize the resulting silanone ligand.[12] In contrast to **2b**, the tungsten analogue of **2b**, [Cp*(OC)$_2$W(SiMe$_3$){O=SiMes$_2$(PNO)}] (**C**), was too unstable to isolate and was readily converted to dioxo(disiloxanoxy)complex [Cp*(O)$_2$W{OSiMes$_2$(OSiMe$_3$)}] (**IV**)[10] in low yield under the reaction conditions.



(1)

Mes = 2,4,6-(CH$_3$)$_3$C$_6$H$_2$

L = DMAP (**2a**), 64%
PNO (**2b**), 64%

The structures of complexes **2a** and **2b** were supported by the elemental analysis data as well as the crystal structure analysis (Figure 1). The overall structure of **2a** is similar to that observed for tungsten analogue **II**.[10] The long Mo···Si(2) distance (3.658(2) Å) and the wide Mo-O(3)-Si(2) angle (155.9(1)°) indicate no direct interaction between Mo and Si(2), i.e., η^1-coordination of the silanone ligand via the oxygen atom. This is also supported by the fact that the Mo–O(3) bond distance (2.178(1) Å) is significantly longer than those of Mo–OSiR$_3$ single bonds (1.89-2.01 Å)[13] and in the shorter range of those of Mo···O=CR$_2$ η^1-coordination bonds (2.18-2.45 Å).[14] The Si(2)–O(3) bond length (1.560(2) Å) is shorter than those of usual Si–O single bonds (1.60-1.66 Å),[15] and comparable to that observed for complex **II** (1.558(4) Å).[10] The bond distance between the silanone silicon (Si(2)) and the coordinated DMAP nitrogen (N(1)) (1.876(2) Å) is also comparable to that in **II** (1.865(5) Å)[10] and much longer than those of usual Si-N single bonds (1.69-1.77 Å).[15] Similar structural characteristics are also perceived in complex **2b**, i.e., η^1-coordination of (PNO)Mes$_2$Si=O to Mo, however the low quality of the crystal prohibited detailed discussion on the structure of **2b** (*R*1 = 0.1302, see ESI).

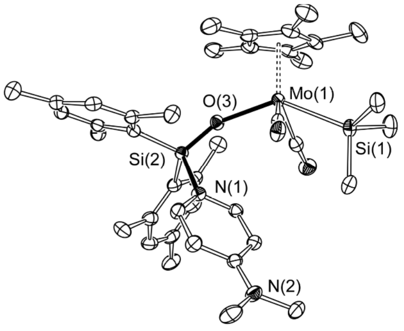
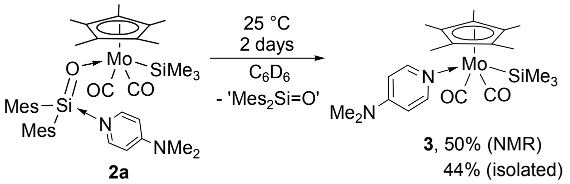


Figure 1. ORTEP drawing of **2a**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are shown below; Mo-Si(1) 2.625(2), Mo-O(3) 2.165(4), Si(2)-O(3) 1.558(4), Si(2)-N(1) 1.865(5), Si(1)-Mo-O(3) 134.81(12), Mo-O(3)-Si(2) 155.3(3).

Complexes **2a** and **2b** show ^{29}Si NMR signals assignable to the Lewis base-stabilized silanone ligand at -22 and -14 ppm and the SiMe$_3$ group at 33 and 32 ppm, respectively. The silanone signals are significantly shifted to higher field than that of the silylene silicon atom in complex **1** (414 ppm)[16] and comparable to that observed for complex **II** (-26 ppm),[10] while the SiMe$_3$ signals are within the usual chemical shift range for Mo-SiR$_3$ complexes (15–36 ppm).[16,17] In the IR spectra, two intense $\nu_{C≡O}$ bands were observed at 1865 and 1770 (**2a**) and 1858 and 1764 (**2b**) cm^{-1}, which are red-shifted about 10-60 cm^{-1} than those observed for complex **1** (1893 and 1828 cm^{-1})[16] and DMAP(silyl) complex [Cp*(OC)$_2$Mo(SiMe$_3$)(DMAP)] (**3**) (1878 and 1796 cm^{-1}, vide infra). These red shifts imply the stronger electron-donating character of η^1-coordinated O=SiMes$_2$(L) ligands in **2** than that of the silylene ligand SiMes$_2$ in **1** and DMAP in **3**.

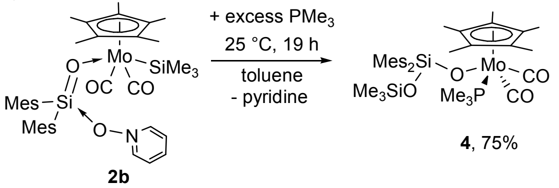
The Lewis bases coordinated to the silanone ligand are readily substituted by free bases in solution. Thus, reaction of DMAP-coordinated complex **2a** with 1 equiv of PNO in C$_6$D$_6$ at 25 °C for 1 h gave an equilibrium mixture of **2a** (18%) and PNO-coordinated complex **2b** (60%). An identical mixture was also formed by the reaction of **2b** with 1.3 equiv of DMAP (**2a** (20%) and **2b** (65%)). These results indicate that coordination ability of PNO to Si in the Mes$_2$Si=O ligand is slightly stronger than that of DMAP.

DMAP-coordinated silanone tungsten complex [Cp*(OC)$_2$W(SiMe$_3$){O=SiMes$_2$(DMAP)}] (**II**) is stable in C$_6$D$_6$ at 25 °C for at least 7 days and decomposed at 80 °C for 3 h to give a complex mixture.[10] In contrast to **II**, molybdenum analogue [Cp*(OC)$_2$Mo(SiMe$_3$){O=SiMes$_2$(DMAP)}] (**2a**) gradually decomposed in C$_6$D$_6$ at 25 °C for 2 days to give DMAP(silyl) complex [Cp*(OC)$_2$Mo(SiMe$_3$)(DMAP)] (**3**) in 50% NMR yield (eq 2). Complex **3** was isolated in 44% yield and characterized by spectroscopic data and elemental analysis, as well as single-crystal structure determination (see, ESI). The transformation from complex **2a** to **3** implies the generation of free silanone 'Mes$_2$Si=O' in the reaction mixture. However, no product derived from the silanone fragment has been identified at all.



(2)

Reaction of DMAP-coordinated silanone tungsten complex [Cp*(OC)$_2$W(SiMe$_3$){O=SiMes$_2$(DMAP)}] (**II**) with 3 equiv of PNO resulted in the construction of the W-O-Si-O-Si fragment to afford disiloxanoxy(dioxo) complex [Cp*(O)$_2$W{OSiMes$_2$(OSiMe$_3$)}] (**IV**) in a moderate yield.[10] In contrast to **II**, DMAP-coordinated Mo complex **2a** gave a complex mixture of decomposed products upon the reaction with excess PNO. No disiloxanoxy complex was detected at all. However, disiloxanoxy(dicarbonyl) complex, *cis*-[Cp*(OC)$_2$Mo{OSiMes$_2$(OSiMe$_3$)}(PMe$_3$)] (**4**), was obtained in 75% yield by thermolysis of PNO-coordinated complex **2b** in the presence of excess PMe$_3$ at 25 °C for 19 h in toluene (eq 3).[18,19] The *cis*-arrangement of two CO ligands in **4** was deduced from the fact that two doublet signals assignable to the CO ligands were observed in the ^{13}C{^{1}H} NMR spectrum (270 ($^2J_{CP}$ = 35 Hz) and 249 ($^2J_{CP}$ = 13 Hz) ppm).[18] The ^{29}Si NMR spectrum showed the resonances for OSiMe$_3$ and OSiMes$_2$ at 3.2 and -36.5 ppm, respectively, which are comparable to those observed for **IV** (11.0 and -33.9 ppm) and those for the reported chemical shifts corresponding to OSiMe$_3$ groups (25 – -5 ppm) and O-SiAr$_2$-O groups (0 – -40 ppm), respectively.[20] In the IR spectrum, two intense CO stretching absorptions were observed at 1931 and 1833 cm^{-1}, which are comparable to those observed for *cis*-[Cp*(OC)$_2$MoX(PR$_3$)] (1970-1928 and 1890-1846 cm^{-1}).[18,19]



(3)

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Notes and references

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†Electronic Supplementary Information (ESI) available: Experimental details for synthesis of **2a**, **2b**, **3**, and **4** and X-ray crystal structure determination of **2a**, **2b**, and **3**. CCDC 1008715 (**2a**), 1008716 (**2b**), and 1008717 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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